# A STUDY OF THE DESTRUCTIVE DISTILLATION OF HARDWOOD SAWDUST IN A FLUIDIZED BED

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A STUDY OF THE DESTRUCTIVE DISTILLATION

OF HARDWOOD SAWDUST IN A FLUIDIZED BED

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# A STUDY OF THE DESTRUCTIVE DISTILLATION OF HARDWOOD SAWDUST IN A FLUIDIZED BED

## Summary

As a result of the great success of fluidized powder techniques in petroleum technology, it was decided to investigate the possibilities of applying a similar technique to wood technology and, in particular, to destructive distillation of hardwood. A review of the literature pointed to the desirability of data in the form of isothermal batch runs at temperatures from 250 to 400 degrees centigrade. An apparatus constructed by R. P. Jongedyk was employed to obtain such data, at five different temperatures, on red oak fluidized with nitrogen. The laboratory experiments indicate that the process is practicable from the point of view of operability, that yields are comparable with those obtained by conventional processes, and that the reaction rates in a fluidized bed are much higher than obtained by present methods for destructive distillation. Both from the point of view of reaction rate and yields of acetic acid and methanol, it seems probable that the optimum temperature of operation is in the neighborhood of 400 degrees centigrade. At temperatures below about 280 degrees centigrade, the reaction appears to be a first order decomposition, with a relatively high temperature coefficient. At temperature above 280 degrees centigrade, the process is apparently controlled by a higher order reaction (perhaps condensation or polymerization), with a re-

latively low temperature coefficient. It is recommended that the laboratory data now available be used to make a rough plant design and cost study, for the purpose of obtaining a semi-quantitative estimate of the commercial possibility of the process.

# Introduction

For many years the hardwood distillation industry was an important producer of methanol and acetic acid. In the period of the first world war the industry reached the peak of its expansion when these two products were in great demand for munitions production. Today the industry is of little importance, since it is unable to compete with the cheaper synthetic products due to high labor costs and high equipment depreciation. Efforts have been made to find some process whereby cheaper types of waste wood, such as sawdust and similar wood waste, might be utilized to improve the economics of the industry.

None of the processes developed has been entirely successful. Wood is a poor conductor of heat and sawdust is even worse since it contains many air spaces which increase the resistance to heat transfer. A stationary mass of sawdust is, therefore, very hard to distill, since it is very difficult for heat to pass through to its center. Some means of agitation must be used in the destructive distillation of sawdust. In the case of mechanical agitation the high temperature of distillation usually introduces complications, while localized overheating is a serious drawback to the rotating retort. Many commercial processes utilizing mechanical agitation, briquetting and similar methods were developed in the period of the first World War. Of these various processes only briquetting is being used commercially today to utilize sawdust.

The success of the recently developed fluidized catalyst process has suggested that it might be possible to distill sawdust successfully

by suspending it in an upward flowing stream of hot inert gas. This technique offers the advantages of excellent temperature control, elimination of localized overheating, and high heat transfer coefficients. R. P. Jongedyk (1) has proposed a new continuous process, employing the fluidized powder technique for the destructive distillation of hardwood sawdust and the gasification of the charcoal produced to supply the inert gas needed as the fluidizing medium. Data on the gasification of carbon with air by the fluidized powder technique has been obtained by workers in the field of coal technology. However, no data exist on the distillation step. Hence an apparatus suitable for experiments on the distillation of wood by this technique has been designed and built by R. P. Jongedyk. The major purpose of this investigation has been to use the apparatus constructed by Jongedyk to obtain as much quantitative information as possible on the destructive distillation of hardwood in a fluidized state.

In addition to the practical need for quantitative data on the distillation step of the proposed new process, there is a second purpose in the investigation of destructive distillation in a fluidized bed. Such experiments may throw some light on the basic mechanism of destructive distillation of hardwood. In the past, the wood has usually been handled in logs and blocks. As the logs were heated, a high temperature developed within them. Consequently, the temperature measurements did not have much significance.

In fluidized bed experiments it appears possible to keep the temperature of the bed fairly constant. If this can be done in a batch

distillation, the data so collected should give real insight into what is going on chemically.

## Literature Survey

The products of hardwood distillation separate naturally according to their solubility and volatility into four groups: charcoal, tar, pyroligneous acid, and gas. The charcoal contains the nonvolatile products, except those carried away mechanically in the vapors, and certain volatile products adsorbed on the charcoal. Klason (2) considers ordinary charcoal to be a primary charcoal plus a secondary deposit of tar coke. The tar is composed mainly of nonvolatile material carried over mechanically in the form of tar fog and of those volatile constituents not soluble in pyroligneous acid. The tars are mostly phenolic in nature and contain a wide variety of these compounds. The pyroligneous acid contains the water soluble volatile constituents and those rendered soluble by the presence of other solvents such as methanol, acetic acid, formic acid, and acetone. Since the pyroligneous acid and the tar form two layers, there is a solubility equilibrium between them and any of the main constituents of one may be found in small amounts in the other. The gas contains the noncondensible constituents but it is also saturated with vapors of the more volatile compounds of the pyroligneous acid and carries a small amount of a fog of the less volatile constituents. The gases most commonly present are carbon dioxide, carbon monoxide, methane, and hydrogen.

The thermochemistry of wood distillation has been widely investigated. Othmer (3) in a recent work on the destructive distillation of maple wood observed several stages of decomposition. Uncombined moisture is evaporated as the temperature is raised to 200 degrees centi-

grade. The first partial decomposition occurs between 200 and 250 degrees centigrade with increasing amounts of tar, gas, and pyroligneous acid being formed. Actual distillation begins at 250 degrees centigrade and becomes more rapid as the temperature increases. The exothermic stage of the distillation in which the lignocelluloses decompose begins at around 275 degrees centigrade. In this stage the greatest amounts of gas and liquid distillates are formed. Klason determined that the exothermic heat of reaction is approximately 6% of the observed total heat of combusion of the wood. He also offered the first partial explanation of the heat given off at this period. By distilling wood under very low pressure, and at a carefully regulated temperature, he found it possible to complete the distillation without obtaining an exothermic reaction. The products of this slow decomposition were, however, different from the original products in that more than 40% of their weight consisted of a transparent red oil, and much less gas and charcoal than usual were formed.

The red oil, when heated to about 275 degrees centigrade, decomposed exothermally, forming considerable quantities of gas, water, a black tar, and coke. This experiment indicated that the first decomposition of wood is not exothermic, but that some of the primary products of the early distillation decompose when heated to the higher temperature.

The distillation is completed for all practical purposes at about 350 degrees centigrade. Above this temperature, gases and tars are the main products with only traces of acetic acid and methanol.

The rate of application of heat controls the transition from one stage to another and influences the final products. Othmer et al, (4) found in their experiments that the maximum methanol peak exists at the same time as the maximum acetic acid peak. The rates of evolution of acetic acid and methanol are controlled by temperature. Increasing the temperature gives an increase in rate and vice versa. Controlled carbonisations, in which the largest part of the distillation is made at the minimum possible temperature and the rate of rise of temperature is kept at a minimum during the critical exothermic stage, gave the largest yields of methanol and acetic acid. In an uncontrolled carbonisation, the yields of charcoal, acetic acid, and methanol are lowered but greatly increased yields of wood gas are obtained.

The sources of the various products of wood distillation have been established (5). Basically, wood is composed of three complex groups: cellulose units, lignin units, and pentosans. The acetic acid is derived largely from the cellulose units, but some is supplied by the decomposition of the pentosans and carbohydrates present in the wood. The methanol is derived solely from the methoxy and acetyl groups attached to the lignin units. Lignin also serves as the source of the large numbers of phenols and phenol ethers that are found in the distillate. Furfural is formed by the thermal decomposition of the pentosans. Gas and tar is formed by the decomposition of the three basic units.

Some data on the physical and chemical properties of red oak (Quercus Rubra), the hardwood chosen for this investigation, exist in

the literature. Merrit and White (6), who studied the partial pyrolysis of red oak in an atmosphere of steam, report a chemical analysis of this type of wood. Another chemical analysis giving the percentages of ash, acetyl, lignin, hemicellulose and alpha cellulose is reported by Wise and Ratliff (7). The various physical properties are summarized in the literature (8).

A great deal of information on the basic properties of fluidization processes is supplied by the work of Parent, Yagol, and Steiner, who experimented extensively with a variety of materials (9). They find that for a given material there should be a balancing of the fine, coarse, and medium fractions for smoothest operation. A preponderance of the coarse materials tends to slug and relatively fine material tends to channel. Some materials, which channel at low velocities, fluidize smoothly at moderate rates. If slugging occurs, it tends to become more violent as the velocities increase. The amount of material in the bed is important. In several instances, material which fluidize well in given bed depths, slug or channel when greater amounts are present. In general, increased bed height accentuates the tendency to slug or channel.

Kalbach (10) develops a method for the application of fluidization batch data to predict the performance of a continuous system. In a continuous process, not all of the particles receive the same treatment. In accordance with the laws of chance, some of the particles in the feed have relatively short residence times within the reactor before being withdrawn in the product while others have relatively long residence

times. This circumstance leads to complications in the mathematical analysis of the data on a continuous operation.

In a batch process, on the other hand, all the particles have the same residence time; and mathematical analysis of the process is relatively simple. Furthermore, from a relatively small amount of batch data it is possible to predict the performance of a continuous unit under a variety of operating conditions.

No data have been found in the literature, on the use of a fluidized system to distill sawdust or on the mechanism of the distillation reaction.

## Experimental Program

Since the main object of the thesis was to study the mechanism of destructive distillation of hardwood in a fluidized bed, the experimental program was designed to eliminate, in so far as possible, all variables except time and temperature. For this reason, it was decided to confine all experiments to one type of wood. Red Oak (Quercus Rubra) was chosen as a readily available hardwood. In order to eliminate variations in size distribution of the particles, it was agreed to prepare a single large batch, which was thoroughly mixed and used as a source of feed in all runs. For the sake of reproducability and ease in control, dry cylinder nitrogen was employed as the fluidizing gas, instead of an attempt to duplicate an industrial setup, in which gas would be obtained from gasification of charcoal from the distillation step. To insure comparable conditions of fluidization in all experiments, the same mass flow rate was employed throughout.

As indicated by the work of Kalbach, discussed in the preceding section, batch runs at constant temperature afford a maximum of information from a minimum of experimental work. Therefore, the program involved a series of isothermal batch runs. As noted in the literature survey, destructive distillation appears to take place in two distinct phases, endothermic reactions occuring below about 275 degrees centigrade, and exothermic reactions occurring at higher temperatures. In order to explore both these regions, it was planned to make runs ranging from about 240 to 400 degress centigrade.

Because of the limitations of time, it was decided not to attempt

a complete chemical analysis of the products. Attention was focused mainly on the products of commercial importance--methanol, acetic acid, and charcoal. In order to obtain a complete material balance, the pyroligneous liquor and gas were also measured. However, it was recognized that an accurate measurement of the gas produced by distillation would be quite difficult, because it is small in amount compared to the fluidizing gas, with which it is mixed. In a preliminary study of this kind it was judged that it was not worthwhile to go to the extreme lengths necessary to measure the distillation gas accurately.

Analysis of the data was organized on the assumption that the most probable mechanism for the thermal decomposition of wood would be a first order reaction. However, the usual equation for a first order reaction involves the amount of undecomposed reactant at any time, whereas the measurable quantities in this case were the amounts of the various products, as a function of time.

Accordingly, the usual equation for a first order reaction was changed into terms of the products, as follows:

$$\frac{dL}{d\theta} = k \left( L_{\infty} - L \right)$$

where: L is the yield of produce at any time

$\theta$ is the time

k is the reaction rate constant

$L_{\infty}$ is the yield of product at infinite time.

This form of the equation shows that if the reaction is first order, a plot of $dL/d\theta$ vs. L should give a straight line. The slope of this line is k, and the intercept on the $dL/d\theta$ axis is the ultimate yield. Thus, this method of plotting the data provides a convenient method of extrapolation to get the ultimate yield. While there was no assurance in advance that the data could in fact be correlated on the basis of a first order reaction, it was felt that the direction and magnitude of such deviations from a straight line as might occur would throw light on the mechanism.

## Experimental Apparatus

The major piece of apparatus used in this work, the reactor, was designed and constructed by R. P. Jongedyk (1). A sketch of this unit is presented in figure 28.

The reactor consisted of three basic units, the reaction vessel proper, the cyclone separator, and a liquid products condenser. The reaction vessel was a four foot section of two inch standard pipe fitted with a slide valve at its lower end. Welded to the top end was a combination expander-disengaging section, constructed of standard five inch pipe, which served to remove some of the sawdust particles carried along in the exit gas stream. Directly above the slide valve at the bottom was a gas expander, which served to break up the inlet gas stream so that smooth fluidization would take place in the reaction vessel. The reaction vessel was heated by means of two electrical heating elements, superimposed on one another and wound around the reaction vessel. The disengaging section and the cyclone separator were heated by an auxiliary circuit, and all three circuits were controlled by Variac Auto-transformers. Five chromel alumel thermocouples in thermocouple wells measured temperatures along the reaction vessel and in the disengaging section. These thermocouple wells extended to the centerline of the vessel.

The cyclone separator was of standard design and was located between the reactor and the liquid products condenser. Its purpose was to remove the remaining sawdust particles in the gas stream before it entered the condenser. Light sheet metal was the material of con-

struction and it was welded throughout. A section of standard 3/4 inch pipe was used to connect the separator to the reaction vessel. The material separated was collected in a bottle at the bottom of the separator. Premature condensation of vapors in the separator was prevented by an electrical heating circuit, an extension of the heating circuit of the disengaging section.

A liquid products condenser, located below the cyclone separator, removed the condensible vapors from the exit gas stream. The condenser shell was constructed of a section of standard four inch steel pipe, fitted with screw caps at either end to facilitate the inspection of the interior. The nineteen condenser tubes were of 5/8 inch diameter 20 gage copper tubing, sixteen inches in length, and were welded to the tube sheet. The temperature of the uncondensed vapors and gases leaving the condenser were measured by a mercury thermometer.

Auxiliary equipment consisted of devices to measure temperature and the gas flow rate. The gas flow rate devices consisted of an inlet flow orifice meter, an exit flow orifice meter and an inclined manometer for measuring the drop in pressure due to friction of the gas flowing through the bed. The pressure taps of the orifice meters were connected to double manometers. The temperature measuring devices were five chromel-alumel thermocouples connected by copper leads to a thermocouple selector switch. The temperatures at the junctions were indicated by a Leeds and Northrup type 8657-C Potentiometer. The thermocouples were checked to within one degree centigrade.

In order to study and find the optimum values for the particle

size range, reactor charge, and gas flow rate, it was necessary to construct an experimental apparatus as similar as possible to the units to be used. A four foot section of glass column, two inches in diameter, and fitted with a disengaging funnel simulated the action of the reactor. A capillary flow meter was calibrated and utilized to meter the inlet fluidizing gas stream. Various size ranges, flow rates and charges were tested. The lowest practicable flow rate for smooth fluidization was determined, so that nitrogen consumption would be at a minimum and vapor condensation could be at a maximum.

From the flow rates studies it was apparent that the original orifice meters on the apparatus were too insensitive to the small flow rates required for fluidization. Smaller orifices were fabricated and substituted after they had been calibrated with a positive displacement meter. At this time the inclined manometer used to measure the friction pressure drop was replaced by a standard upright manometer, which was considerably easier to read.

The results from the first two runs indicated that the exit orifice meter was still too insensitive to measure accurately the fluctuating extremes of the exit flow rate. This orifice meter was then replaced with a capillary type meter. This meter consisted of a section of capillary tubing, approximately 1-1/2 m.m. in diameter and 28 inches in length, connected to the same double manometer which had been used with the exit orifice meter. The capillary meter was calibrated with a positive displacement meter and then connected to the exit gas outlet of the liquid products condenser by a length of thick rubber tubing.

In the center of this rubber tubing was a "T" type fitting, the bottom leg of which was fitted with a short piece of rubber tubing and a spring clamp. This arrangement was so devised as to permit the removal of gas samples for analytical purposes during the course of each run.

The gas samples were analyzed with a standard type Orsat gas analyzer. The units composing the model were a carbon dioxide absorption pipette, an oxygen absorption pipette, a copper oxide carbon monoxide converting tube and a combustion pipette with a heating element for burning hydrocarbon gases. A saturated salt solution was originally used as the containing fluid but gave erratic results in the first two runs. It was thought that the carbon dioxide was being absorbed in the salt solution, and, since the amount in the gas stream was small, the error introduced was significant. Mercury was then introduced as the containing fluid. All runs afterthe first two were made with mercury instead of the saturated salt solution.

## Experimental Procedure

The preparation of an adequate quantity of sized sawdust was the first step undertaken. Two sections of dressed lumber , 12'x4"x4", were obtained from an Atlanta lumber yard. These sections were sawed into pieces approximately four feet in length and turned to shavings and chips on the lathe located in the Chemical Engineering shop. A small rotating hammer mill, belonging to the Ceramic Engineering Department, was utilized to reduce these shavings and chips to sawdust. The sawdust so obtained was screened on a Tyler Rotap Machine, using a set of standard Tyler wire screens.

The major portion of the prepared sawdust was found to pass 42 mesh and was retained on 250 mesh screens. This size range fulfilled the distribution requirements for smooth fluidization as outlined by Parent, Yagol, and Steiner. When tested in the experimental glass column at reactor flow velocities of 0.5 to 1.0 foot per second, no slugging or channeling was noted. It was decided, therefore, to use this size range and a reactor velocity of between one half and one foot per second of nitrogen. A size analysis of the sawdust as to fractions is given under the results.

The experimental glass column was also used to determine the maximum weight of charge to be distilled in each run. This seemed to be justified, as the volumes of the glass column and the reaction vessel were approximately the same. It was noted that when the bed weight exceeded 500 grams there was a strong tendency towards slugging. To insure smooth fluidization a maximum charge of 400 grams of sawdust was decided

upon. One run was made with a charge of 500 grams without any appreciable slugging noted, but all other runs were made with 400 grams of charge.

In preparation for a distillation run the first step was to raise the reactor temperature to the desired level. Experience gained from two preliminary runs indicated that the introduction of the cold charge of sawdust into the hot reactor caused a large drop in temperature of the thermocouple at the center of the reactor. It was found necessary to raise the temperature at this thermocouple, the second from the bottom of the reactor, to approximately 75 degrees above the desired operating level before the charge was introduced. The temperature of the reactor was controlled by means of the Variac Autotransformers. The maximum rate of temperature rise was approximately 150 degrees centigrade per hour. The reactor temperature was very sensitive to changes in voltages induced across the heating elements and a minimum of manipulation was required to maintain the temperature at the level desired once the run had begun.

Dry nitrogen was admitted to the reactor at a slow rate as the reactor temperature was being raised. This served to sweep out any oxygen remaining in the reactor and prevent oxidation of the charge. The nitrogen was supplied from high pressure cylinders, and the flow rate was controlled by means of a reducing valve attached to the cylinder. The flow rate was increased before the actual run was started, and a small amount of gas was allowed to flow into the reactor through the pressure taps to prevent their being clogged with sawdust once the run was started.

The inlet flow rate of nitrogen gas was kept constant during the runs, and the same rate was used in all runs.

Cooling water was allowed to circulate through the liquid products condenser while these other preparations were being made. The condenser was thus brought to its approximate operating temperature before the beginning of the run.

When the reactor temperature had reached the operating level sought, the sawdust charge was introduced at the top of the reactor by means of the hopper valve arrangements previously described. Almost instantly, a great surge of vapor and gas was indicated by the action of the manometers. Within one to three minutes after the introduction of the charge the first drop of distillate left the condenser. The runs were timed with the first drop of distillate indicating zero time as this was the first measurable formation of product. The reactor temperature, as a rule, dropped to the operating level after two to three more minutes had passed. Temperature readings of all five thermocouples were taken at intervals of five minutes, and any change at thermocouple number two was compensated by manipulations of the Variac Controls.

Samples of liquid distillate were taken every five minutes for the first thirty to forty minutes of the run. As soon as the amount of distillate collected in a five minute interval tended to become negligible, the collection interval was increased to ten minutes. The liquid samples were collected in small weighing bottles, as the amount collected, even at the start, rarely exceeded forty grams in weight. The gas samples were collected as fast as they could be analyzed. The analysis

of the gas was limited to carbon dioxide and carbon monoxide as these two gases were the main constituents and this served to speed up the gas analysis. The minimum number of gas samples analyzed during any one run was three. Sheet metal sample flasks were used for the first two runs to collect the gas samples. These proved to be unsatisfactory due to leakage and difficulty in drawing the samples into the Orsat apparatus. By utilizing ordinary toy balloons fitted with rubber stoppers and glass stopcocks a more efficient method of sampling was devised. These balloons could be completely evacuated of air by a low vacuum, and the entering gas sample from the reactor inflated them very easily. The samples could be pulled into the Orsat apparatus with little likelihood of contamination.

At regular intervals during each run, readings were taken of the exit flow manometer, the static pressure at the inlet orifice, and the pressure drop due to friction across the bed. Readings were taken at less frequent intervals of the liquid products condenser temperature and the inlet gas temperature. Both these temperatures were measured by means of mercury thermometers placed in the gas stream.

The runs were ended when the distillate collected in a ten minute period was negligible in quantity. When this was noticed, the reactor heating circuits were shut down; and the reactor was allowed to cool. To prevent the oxidation of the residue which would occur when the hot charcoal came in contact with the atmospheric oxygen, the reactor residue was allowed to cool below 150 degrees centigrade before it was removed from the reactor and weighed.

After the collected distillate had been weighed, it was analyzed

for acid and methanol content. The total acidity was determined instead of analyzing for acetic and formic acids. This seemed to be advisable, as an involved and tedious procedure would have been necessary to separate the two acids. According to the literature, the formic acid is always a small fraction of the acid present at any time. A small amount of the distillate, about 0.3 grams, was placed in a 250 cubic centimeter Erlermeyer flask. To this was added 100 cubic centimeters of distilled water and five drops of phenolphthalein indicator solution. The resulting solution was titrated with a standard solution of aqueous sodium hydroxide. The titration to the neutral color was made possible by placing a daylight fluorescent lamp directly behind the flask being titrated. A procedure similar to this was used by Othmer (4) with the exception that he used phenolphthalein as an outside indicator. The amount of acid was expressed in milliequivalents, which made no distinction as to the source of the acidity.

The methanol analysis used was suggested by the procedure of Othmer (4). He made 100 cubic centimeters of raw settled liquor strongly alkaline with sodium hydroxide and distilled it. By the time 25 cubic centimeters had been distilled the temperature was always high enough to assure that all the alcohol had been removed. The combined distillate samples in this work rarely exceeded 50 grams, with only one individual sample weighing more than 25 grams. It was necessary, therefore, to combine three or more samplesto have an amount sufficiently large to distill. These combined samples were made strongly alkaline by the addition of 25 grams of solid sodium hydroxide and one fourth of their

volume was distilled over. In all cases the solution temperature was over one hundred degrees centigrade by the time that this amount had distilled over. The water-methanol distillate was weighed and its density was determined by a one cubic centimeter pipette fashioned into a pycnometer and calibrated with distilled water. Traces of acetone and other low boiling compounds present in wood distillates would introduce a small error into this type of analysis, but it is not thought that this error could be significant (4).

A standard procedure for moisture determination was used in this work. The samples were heated at 100-105 degrees centigrade until there was no further loss in weight. This was found to occur in a period of from six to eight hours.

## Results

The characteristics of the sawdust used are summarized below:

Species: Red Oak (Quercus Rubra)

Moisture: 6.4%

Size Analysis:

Size Range 42 - 250 mesh

54.75% - passing 42 mesh, retained on 80 mesh

15.10% - passing 80 mesh, retained on 100 mesh

13.32% - passing 100 mesh, retained on 150 mesh

9.47% - passing 150 mesh, retained on 200 mesh

6.31% - passing 200 mesh, retained on 250 mesh

1.05% - passing 250 mesh

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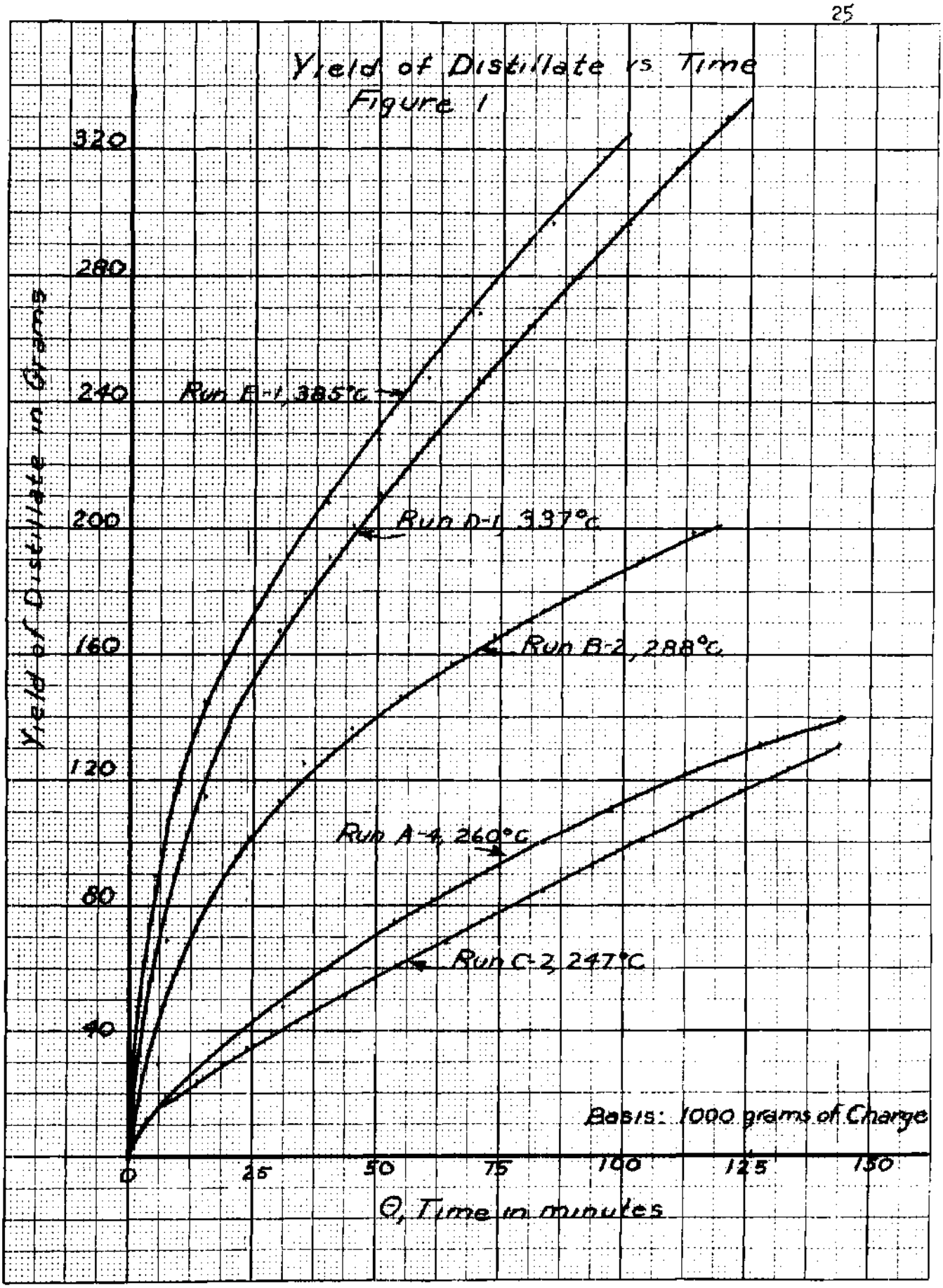
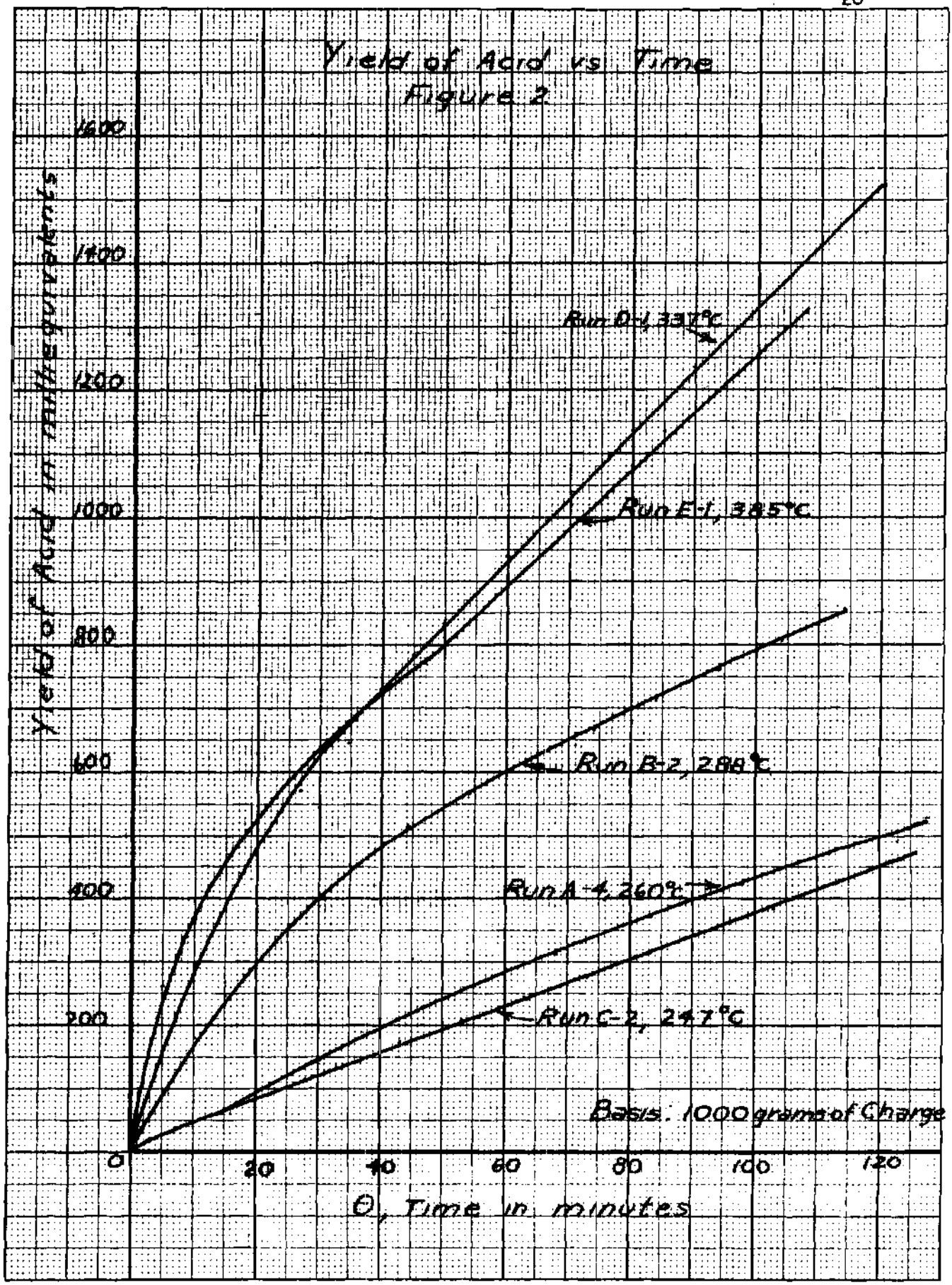
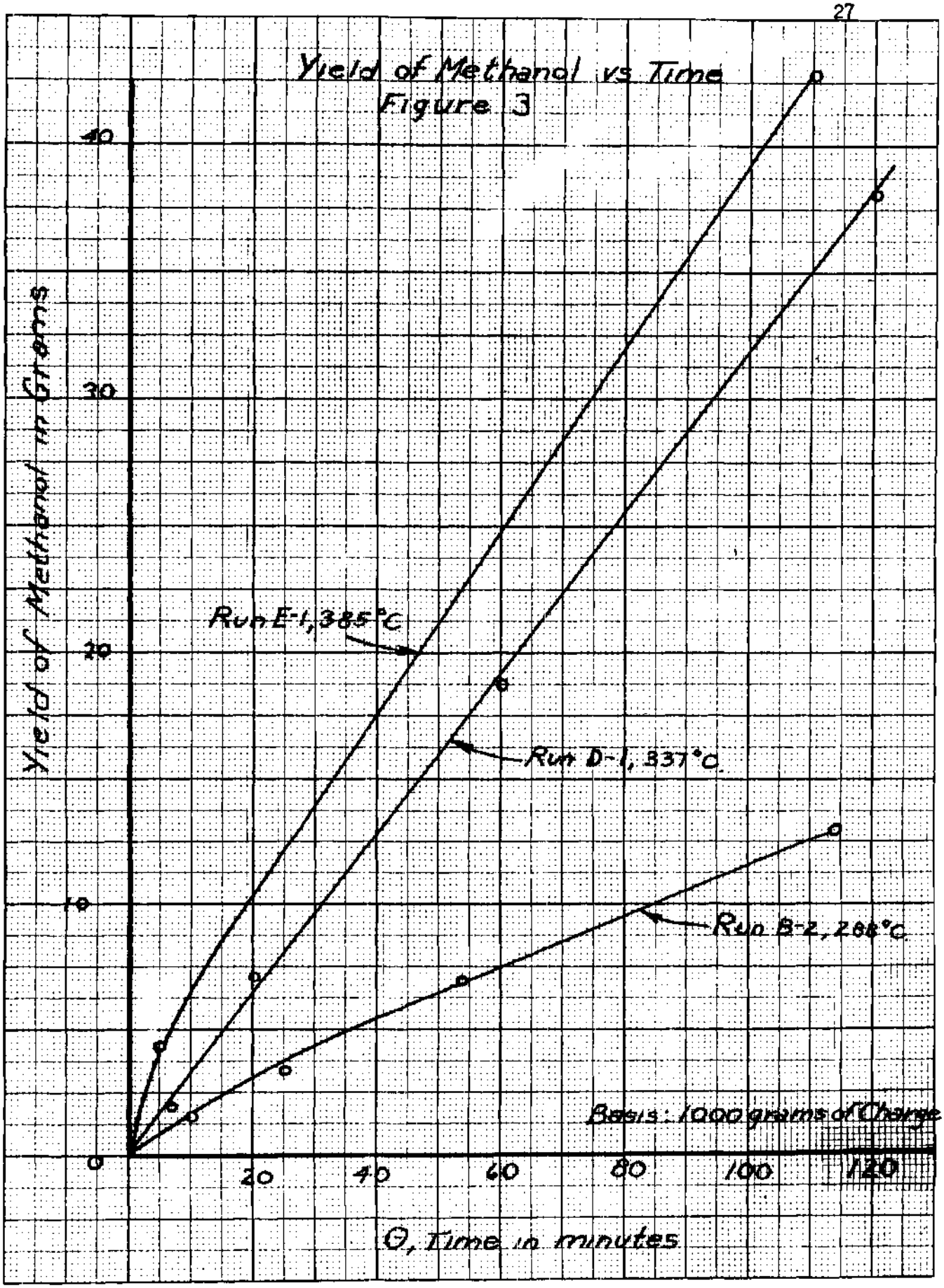
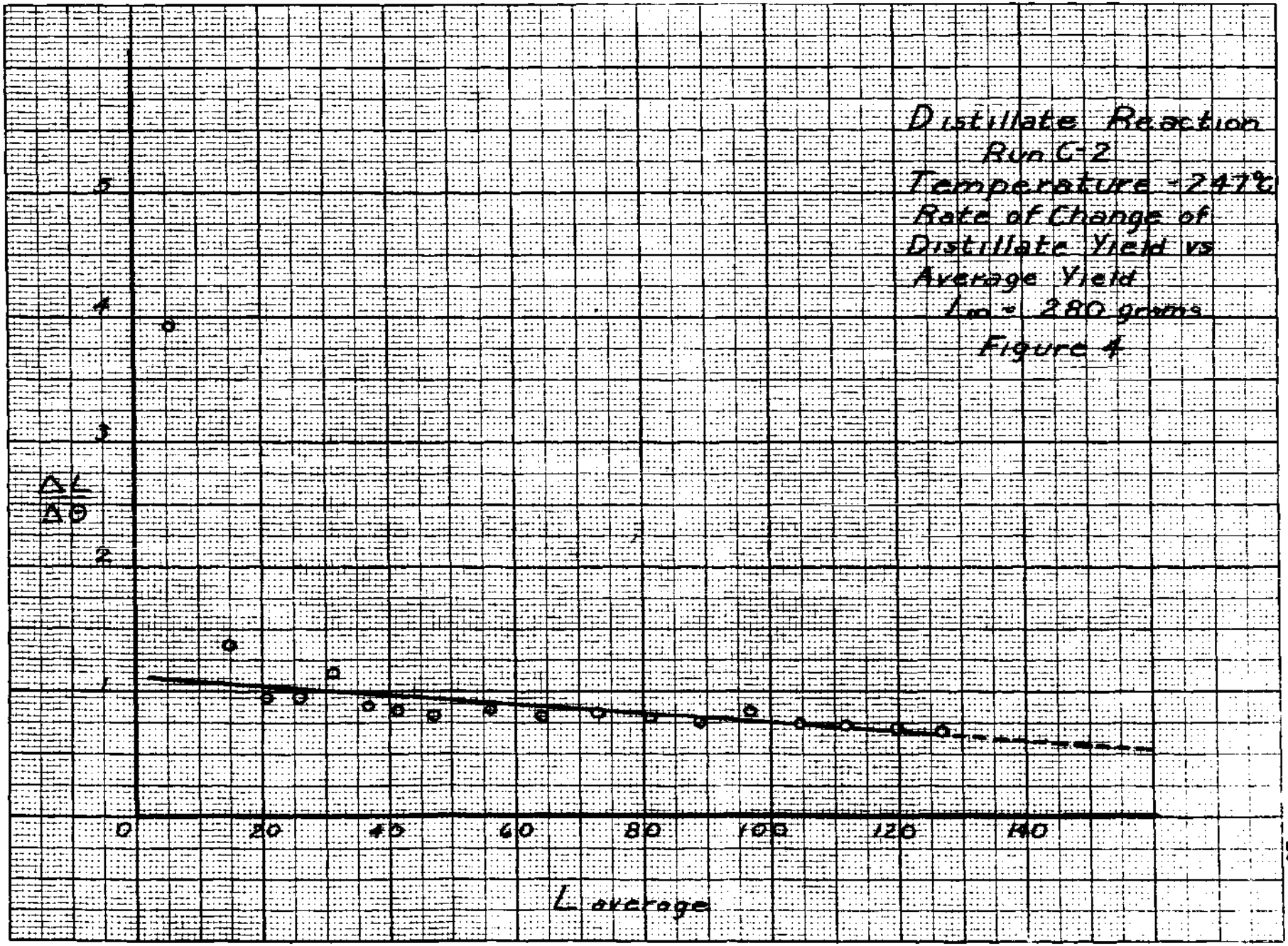
100.00%

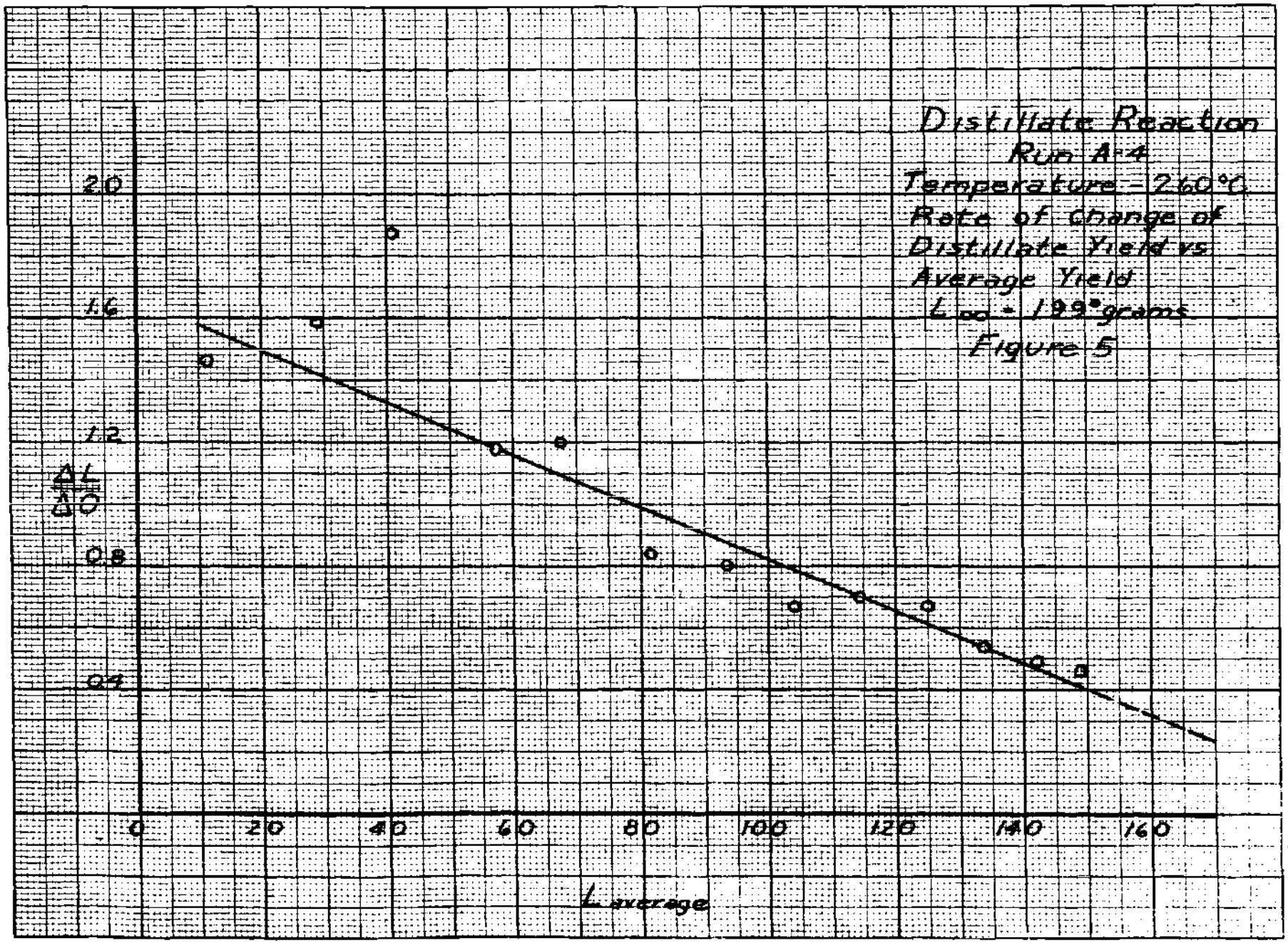

Yield of Distillate vs Time
Figure 1
320
280
240
200
160
120
80
40
Yield of Distillate in Grams
Run E-1, 385°C
Run D-1, 337°C
Run B-2, 288°C
Run A-4, 260°C
Run C-2, 247°C
Basis: 1000 grams of Charge
0
25
50
75
100
125
150
Θ, Time in minutes

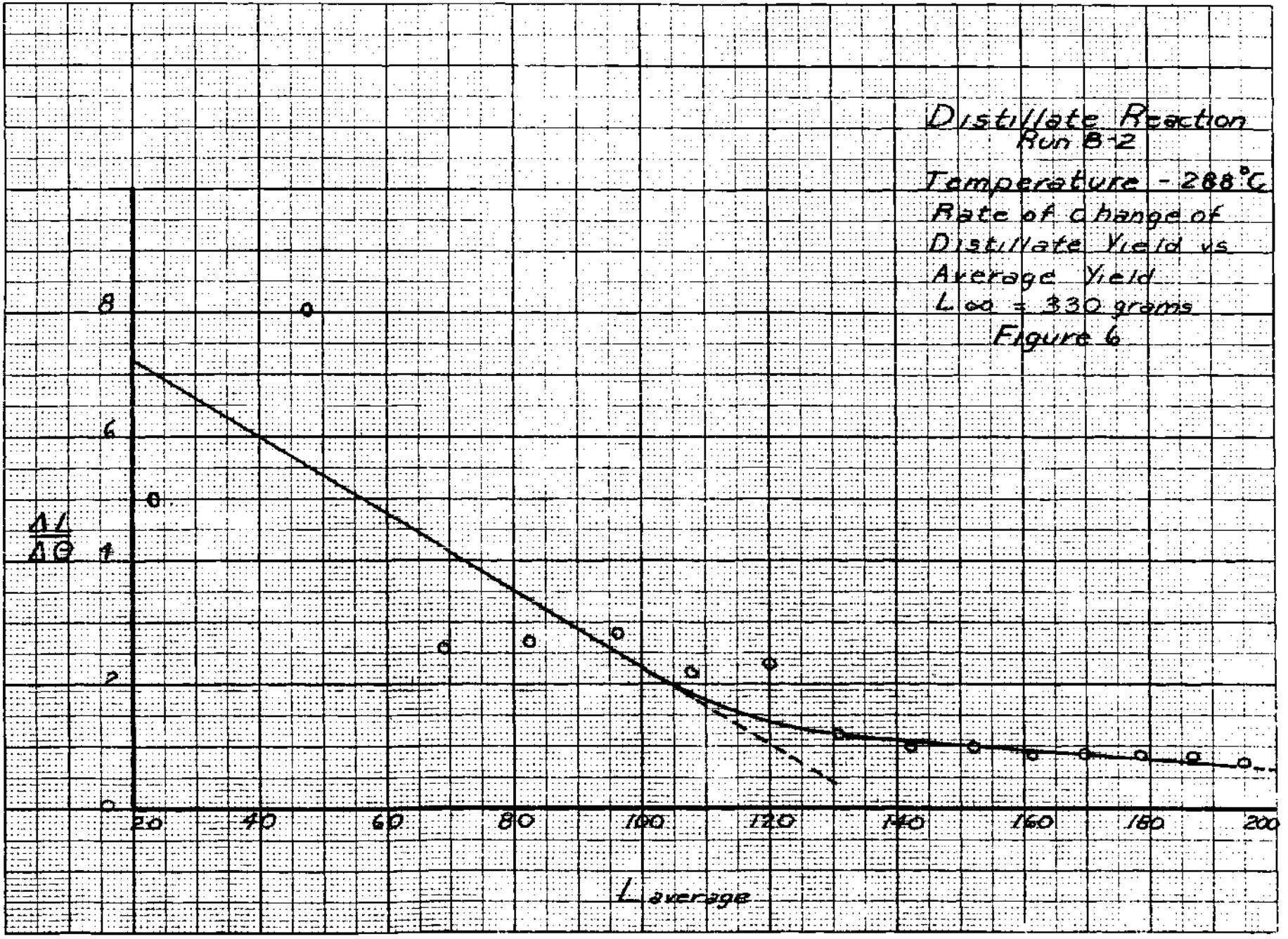

Yield of Acrol vs Time
Figure 2
Yield of Acrol in milliequivalents
1600
1400
1200
1000
800
600
400
200
0
Run D-1, 337°C
Run E-1, 385°C
Run B-2, 288°C
Run A-1, 260°C
Run C-2, 247°C
Basis: 1000 grams of Charge
0
20
40
60
80
100
120
θ, Time in minutes

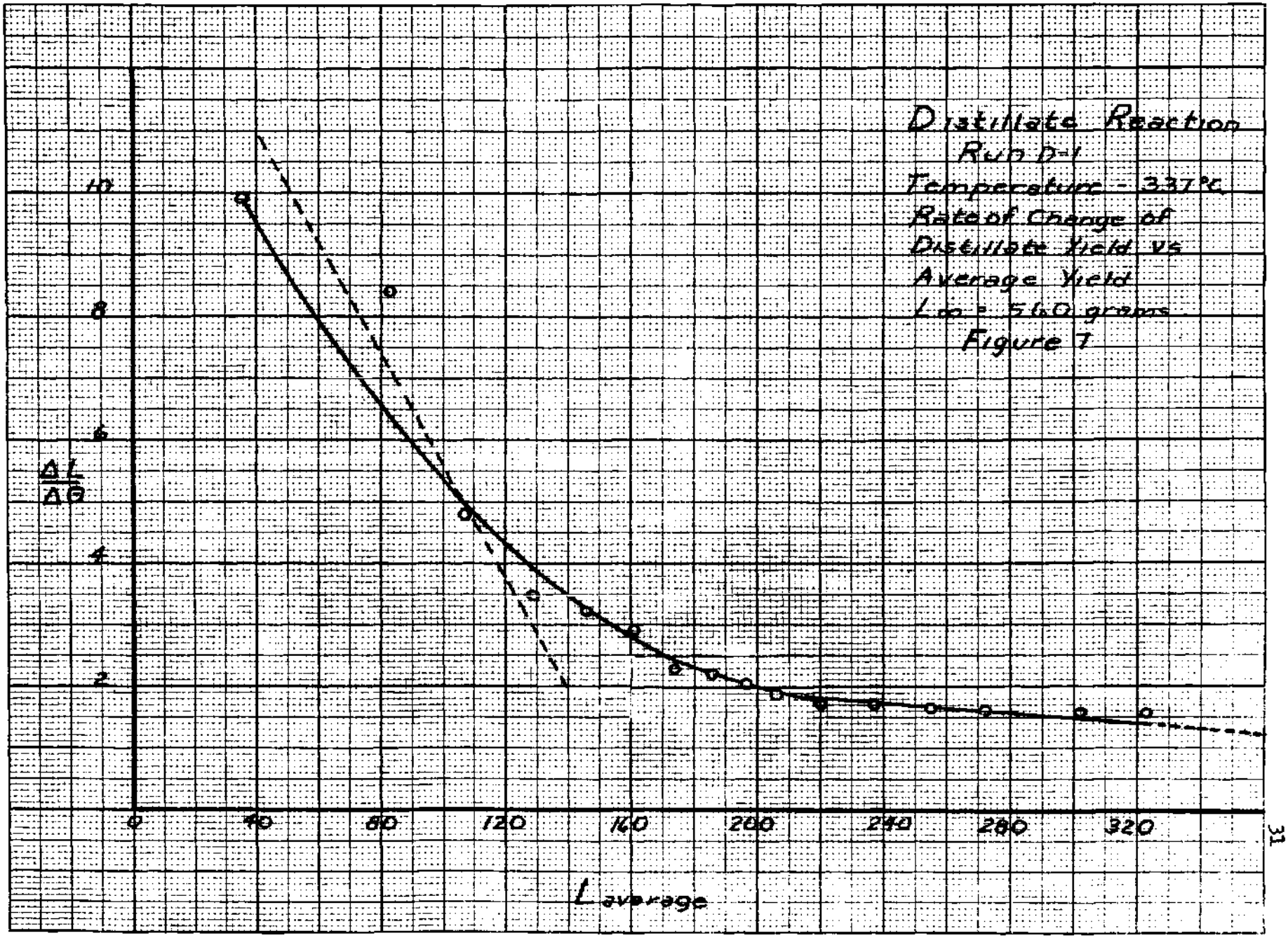
Yield of Methanol vs Time
Figure 3

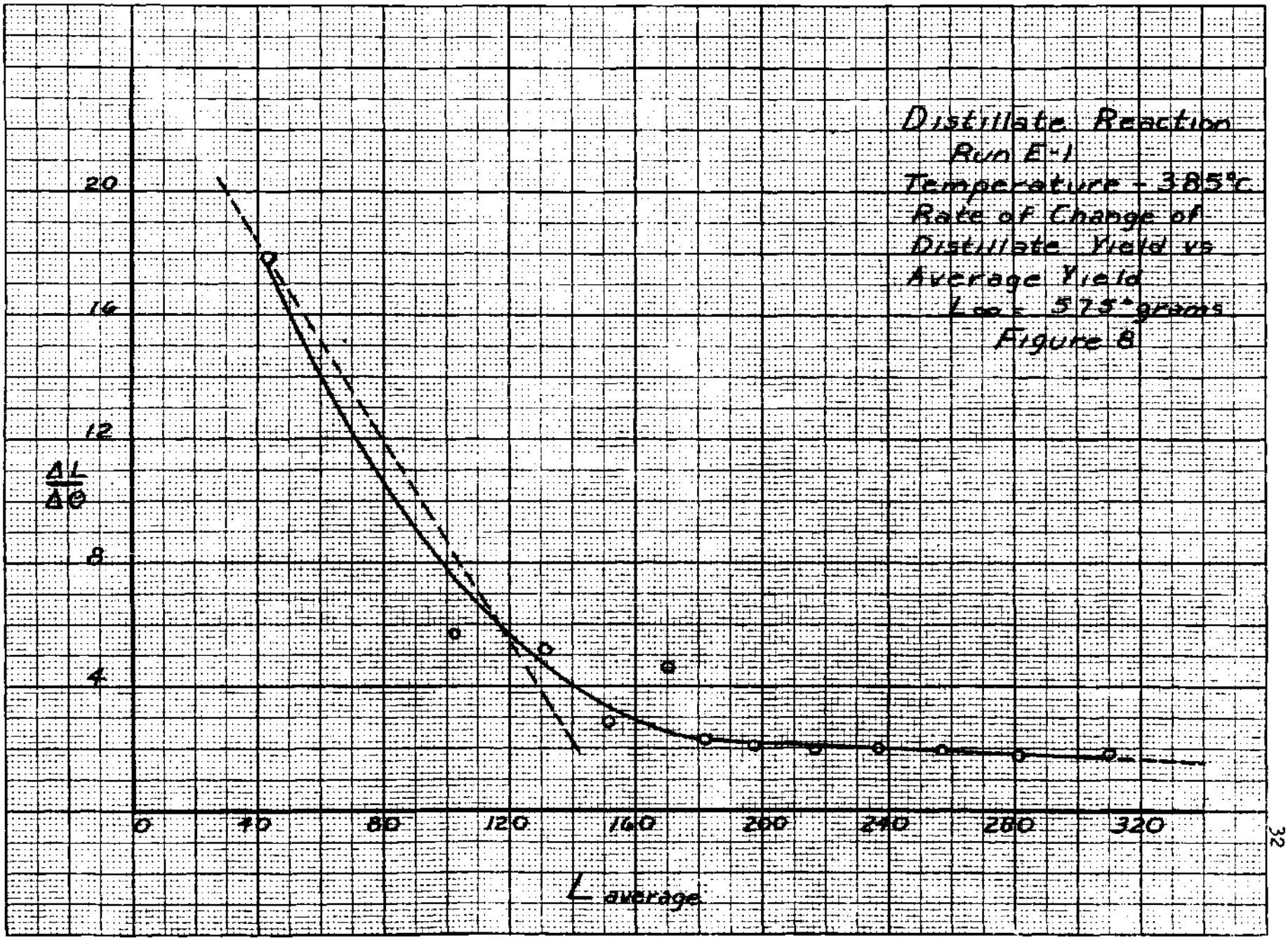


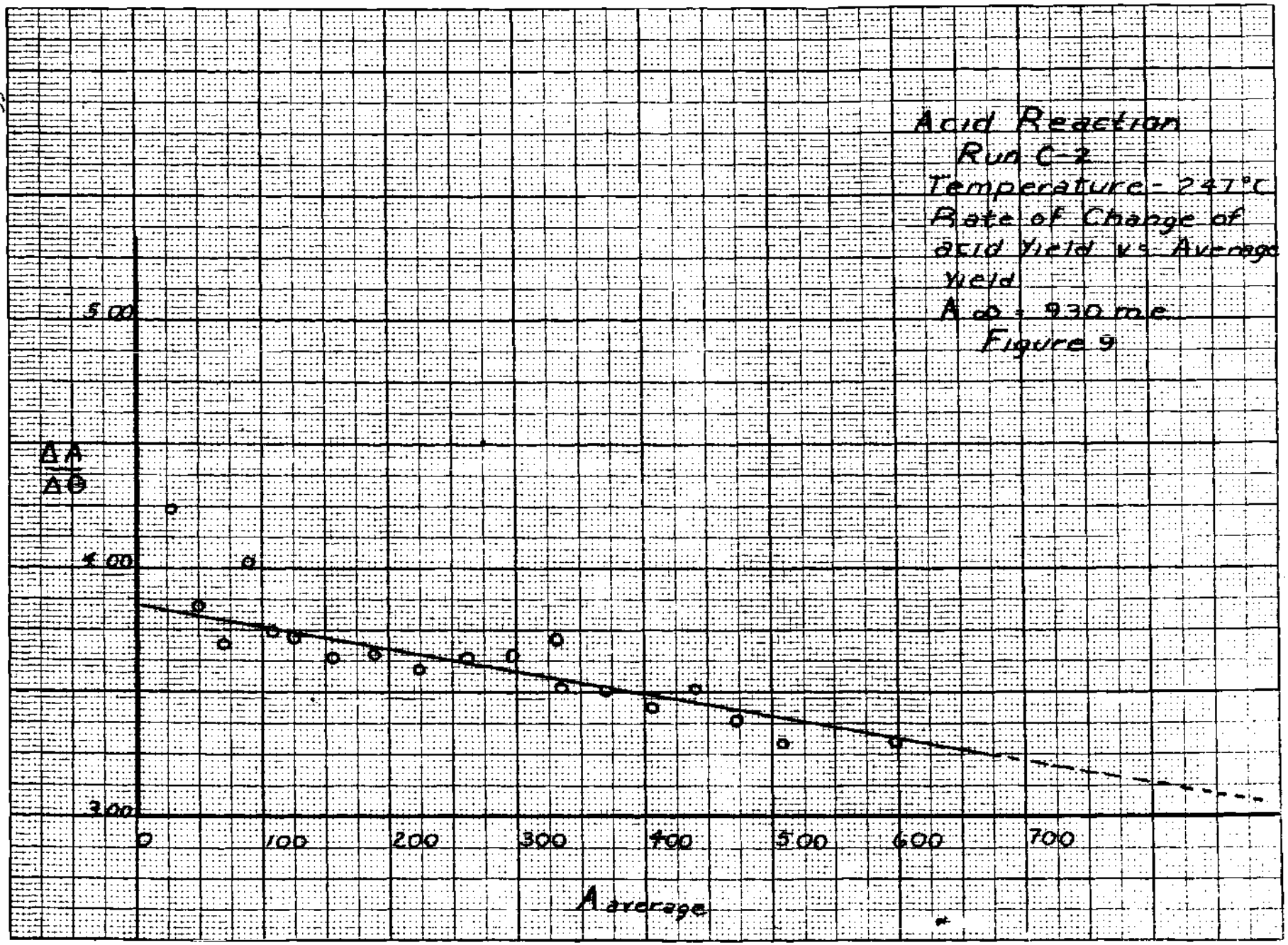

Distillate Reaction
Run C-2
Temperature -247°C
Rate of Change of
Distillate Yield vs
Average Yield
1 cm = 280 grams
Figure 4
5
4
3
2
1
Δ L / Δ θ
0
20
40
60
80
100
120
140
L average

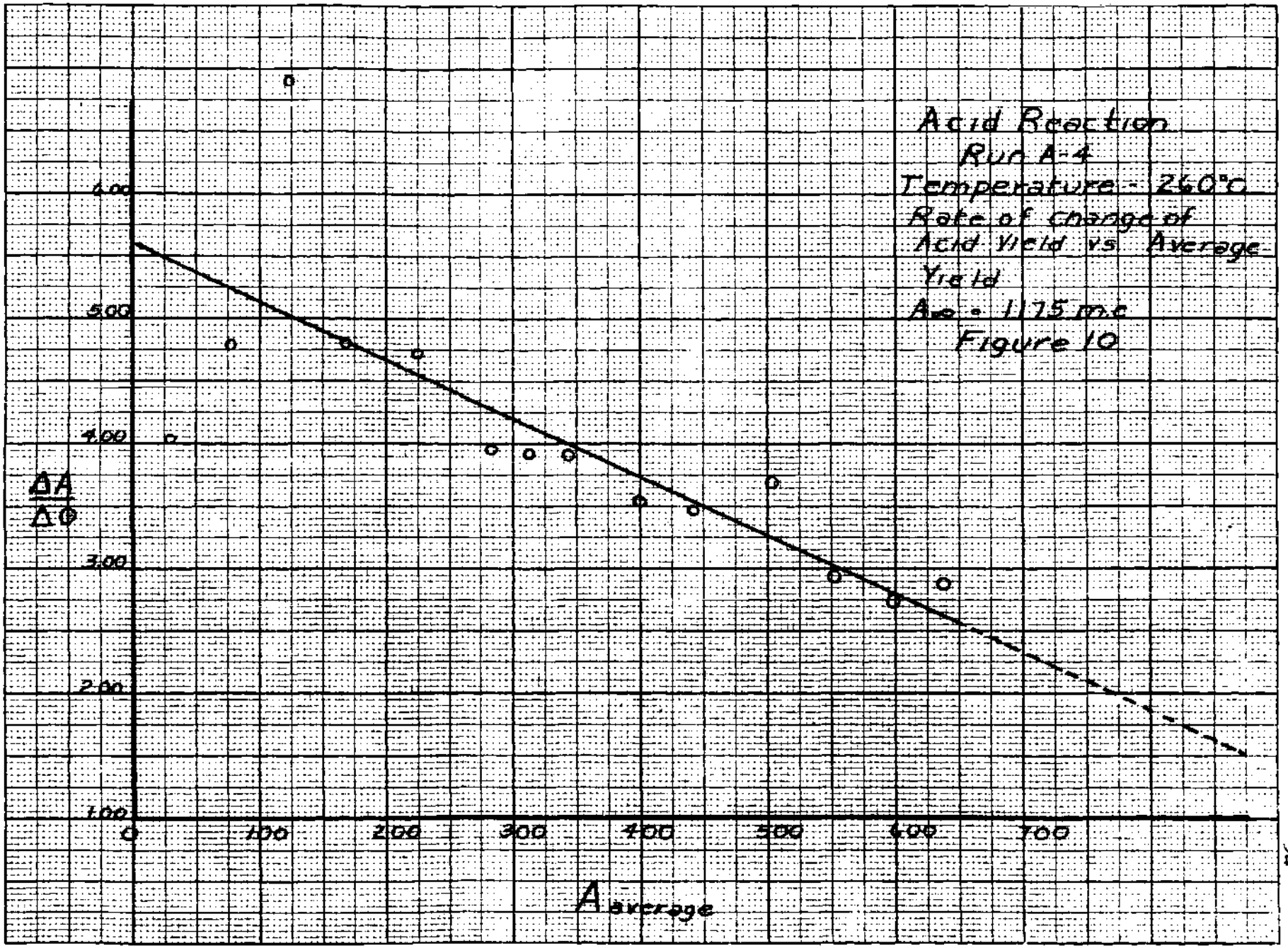

Distillate Reaction
Run A-4
Temperature = 260°C
Rate of Change of
Distillate Yield vs
Average Yield
L∞ = 199* grams
Figure 5
2.0
1.6
1.2
ΔL/Δθ
0.8
0.4
0
20
40
60
80
100
120
140
160
L average

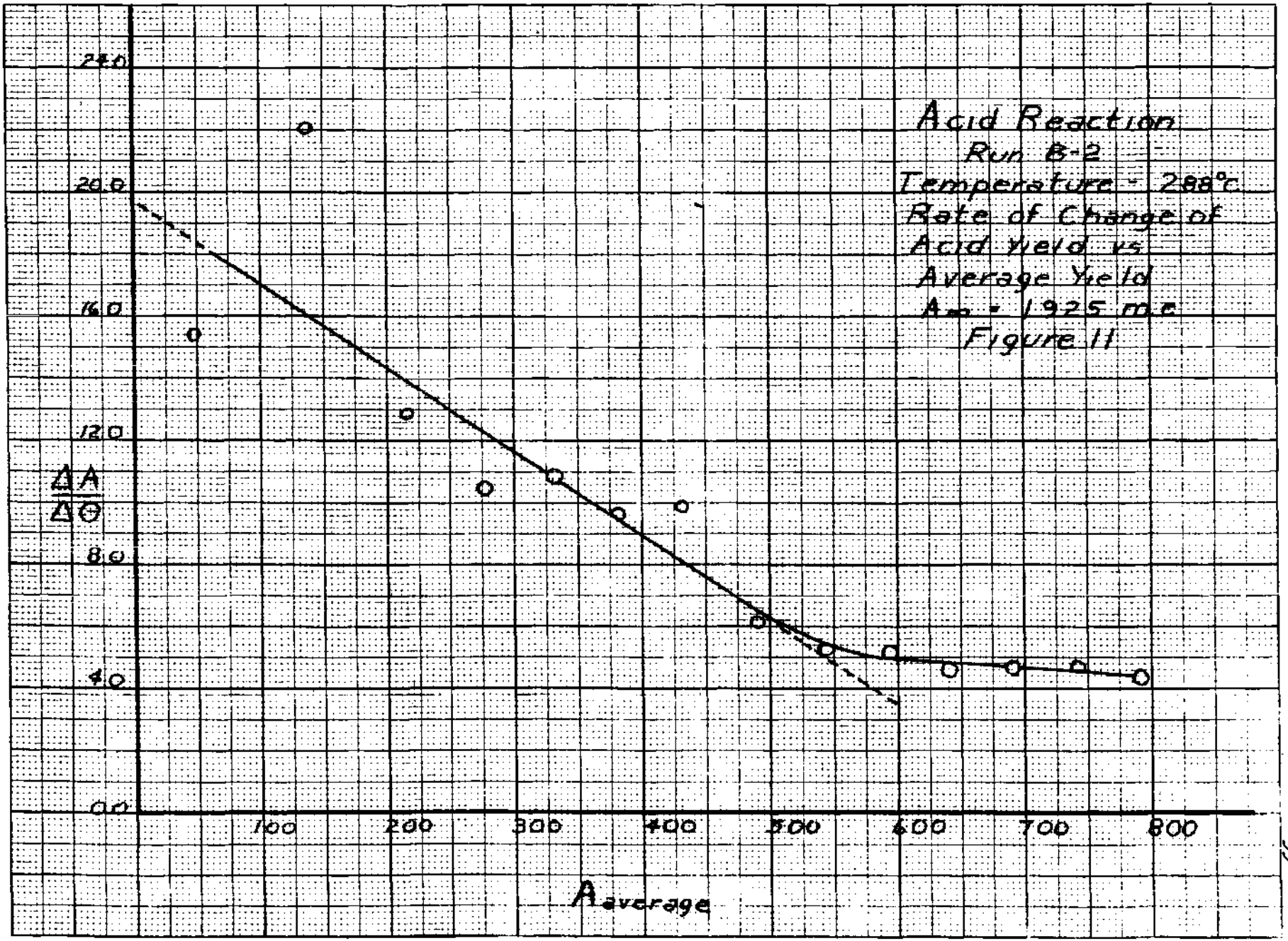

Distillate Reaction
Run B-2
Temperature - 288°C
Rate of change of
Distillate Yield vs
Average Yield
L∞ = 330 grams
Figure 6
8
6
4
2
0
ΔL/ΔΘ
20
40
60
80
100
120
140
160
180
200
L average

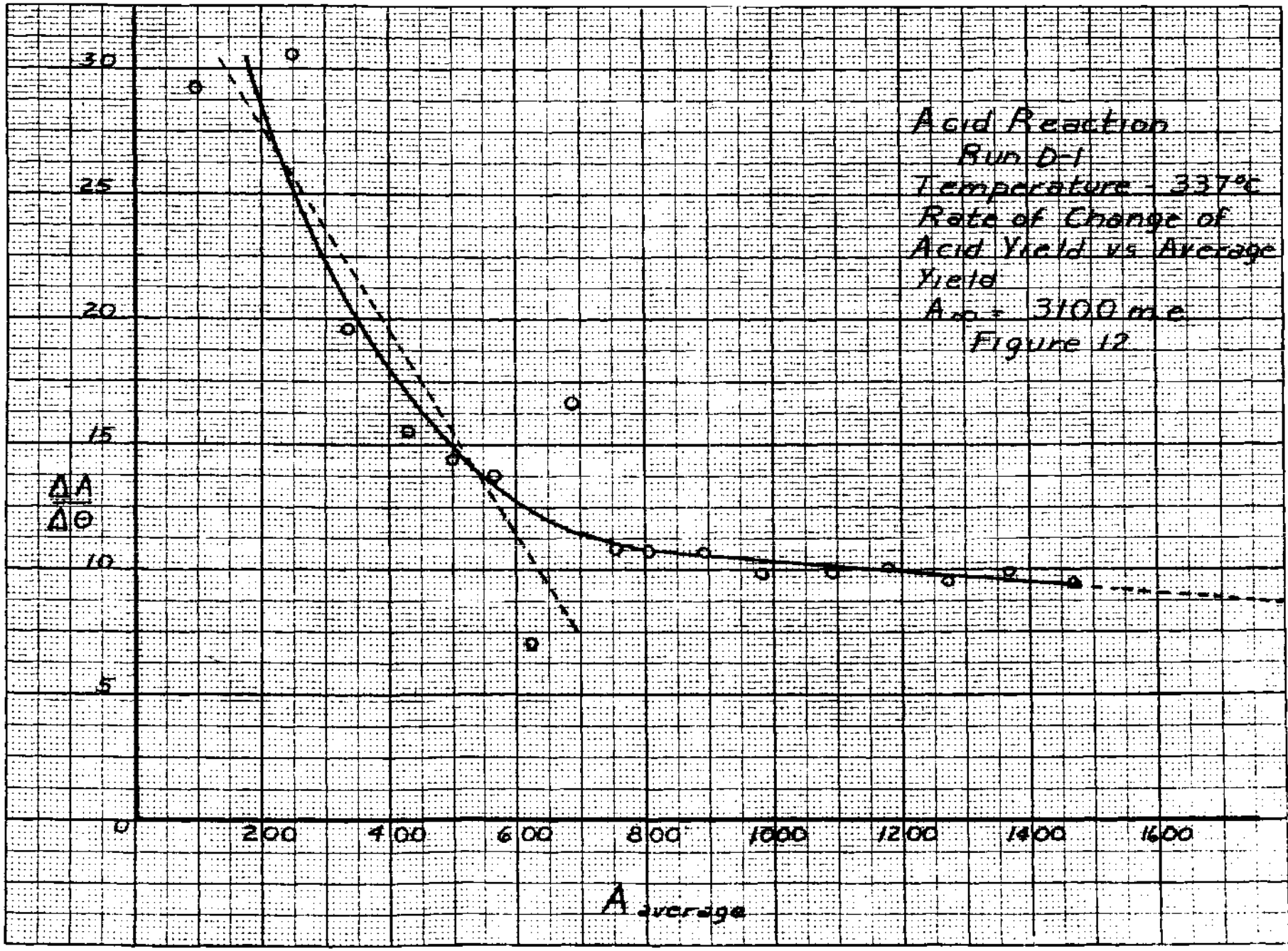

Distillate Reaction
Run D-1
Temperature - 337°C
Rate of Change of
Distillate Yield vs
Average Yield
L∞ = 560 grams
Figure 7
10
8
6
4
2
ΔL/Δθ
0
40
80
120
160
200
240
280
320
L average

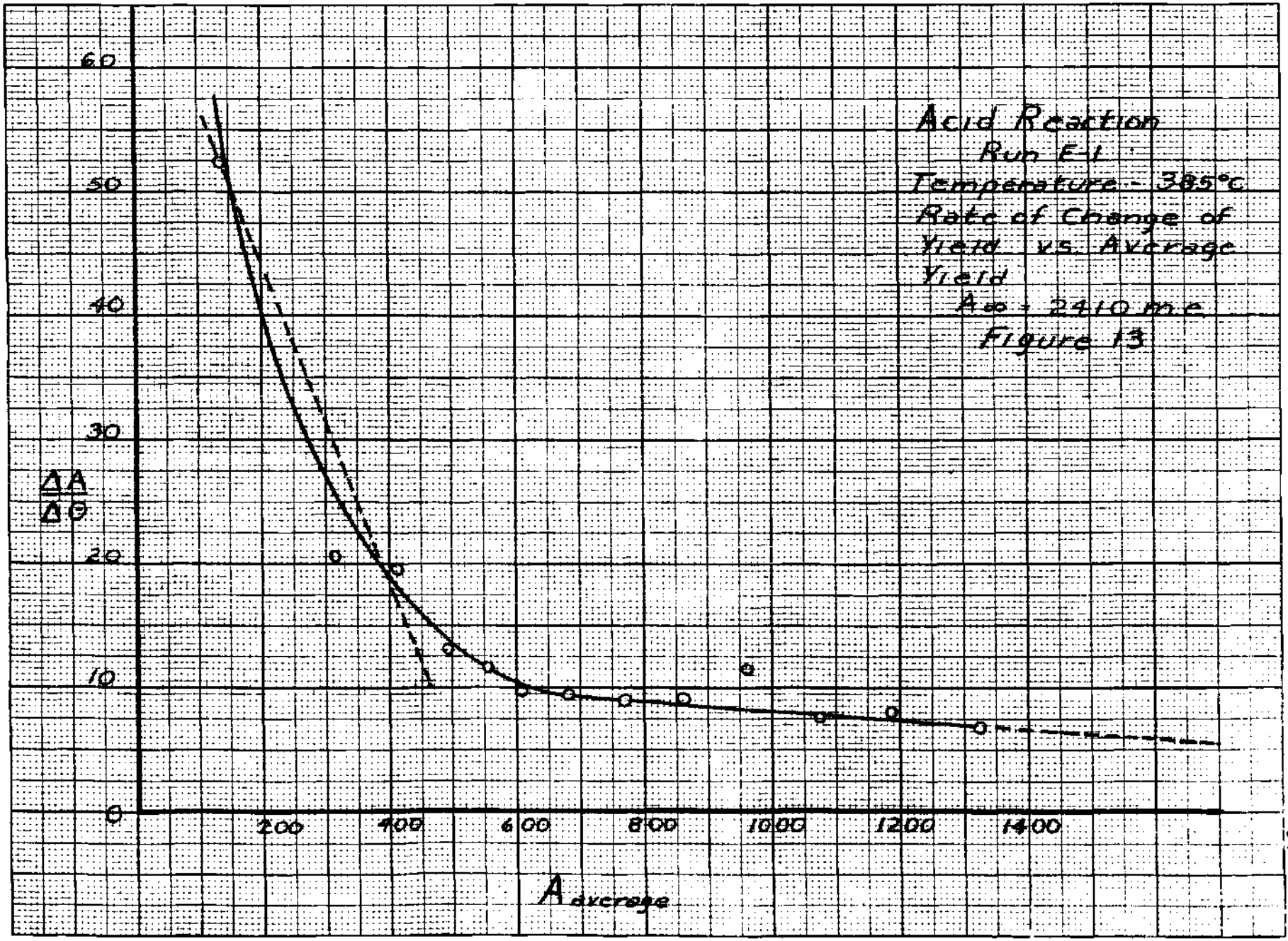

Distillate Reaction
Run E-1
Temperature - 385°C
Rate of Change of
Distillate Yield vs
Average Yield
Loo = 575* grams
Figure 8
20
16
12
ΔL/Δθ
8
4
0
40
80
120
160
200
240
280
320
L average

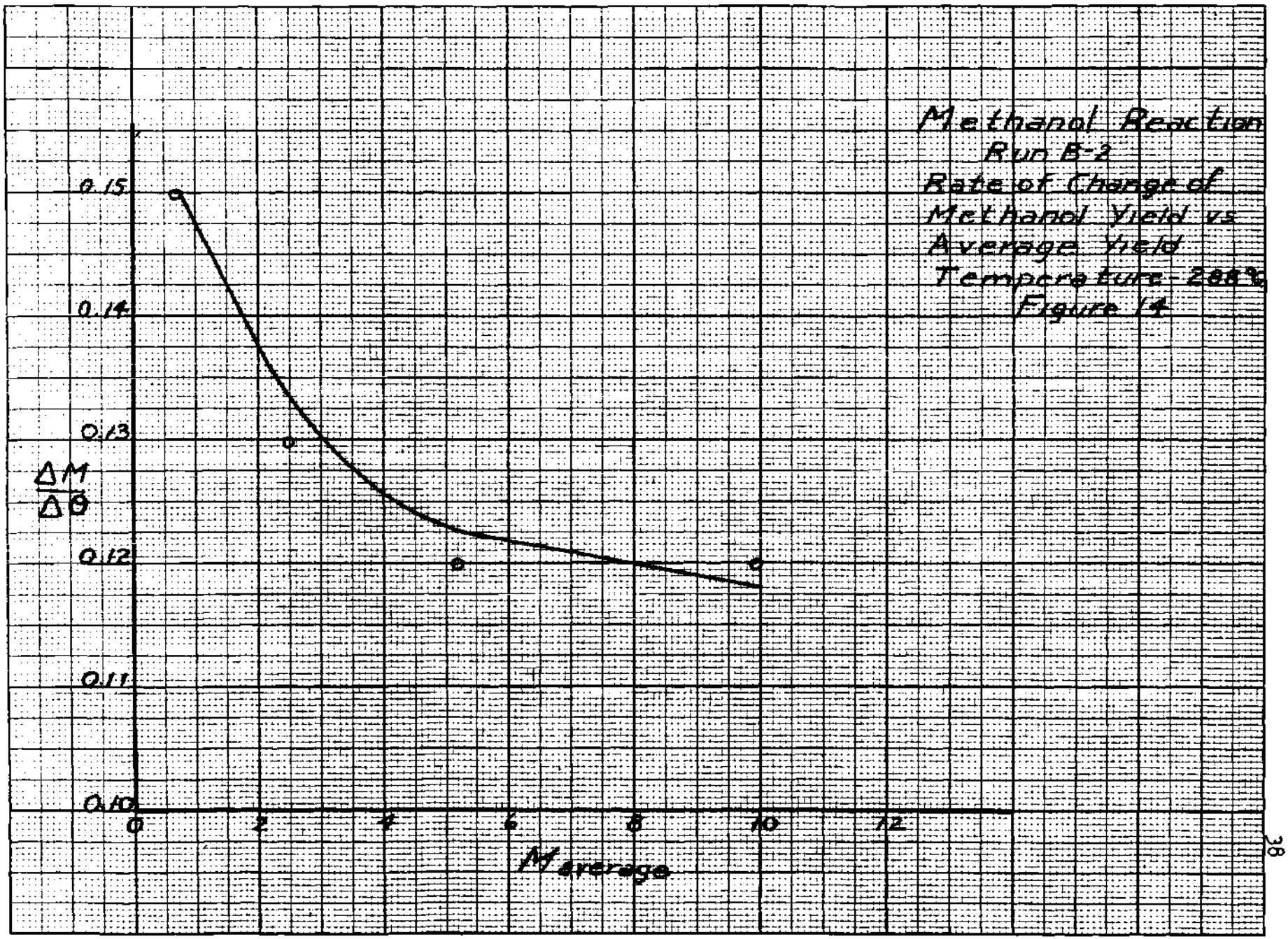

Acid Reaction
Run C-2
Temperature - 247°C
Rate of Change of
acid yield vs. Average
yield
A∞ = 930 m.e.
Figure 9
ΔA/Δθ
5.00
4.00
3.00
0
100
200
300
400
500
600
700
A average

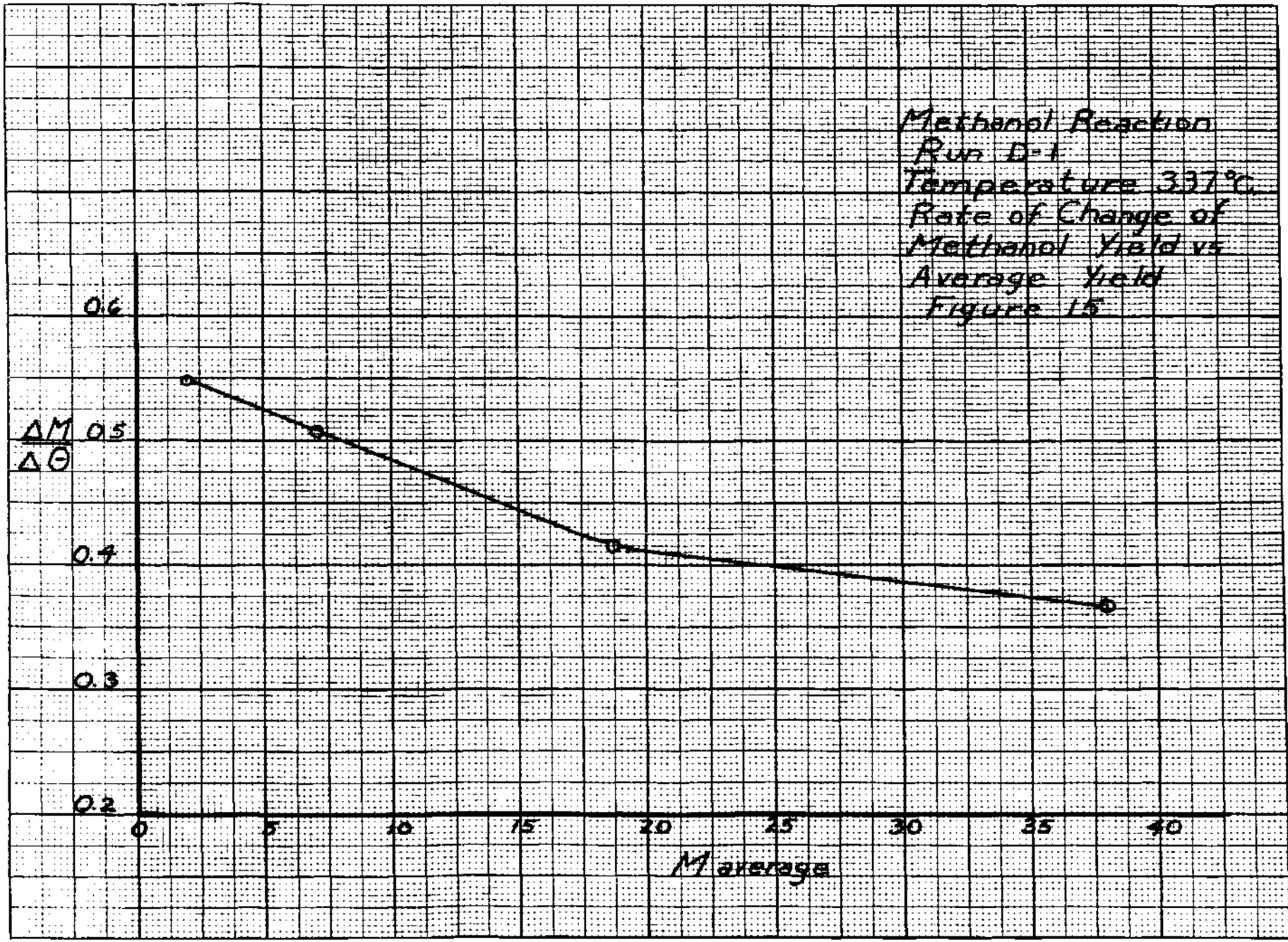

Acid Reaction
Run A-4
Temperature - 260°C
Rate of change of
Acid Yield vs. Average
Yield
Ao = 1175 m.e
Figure 10
4.00
5.00
4.00
3.00
2.00
1.00
ΔA/Δθ
0
100
200
300
400
500
600
700
A average


Acid Reaction
Run B-2
Temperature - 288°C
Rate of Change of
Acid Yield vs
Average Yield
A∞ - 1925 m.e
Figure 11
240
200
160
120
80
40
00
ΔA/Δθ
100
200
300
400
500
600
700
800
A average


Acid Reaction
Run D-1
Temperature - 337°C
Rate of Change of
Acid Yield vs Average
Yield
$A_{\infty}$ = 3100 m e
Figure 12
30
25
20
15
10
5
0
$\frac{\Delta A}{\Delta \theta}$
200
400
600
800
1000
1200
1400
1600
$A_{average}$

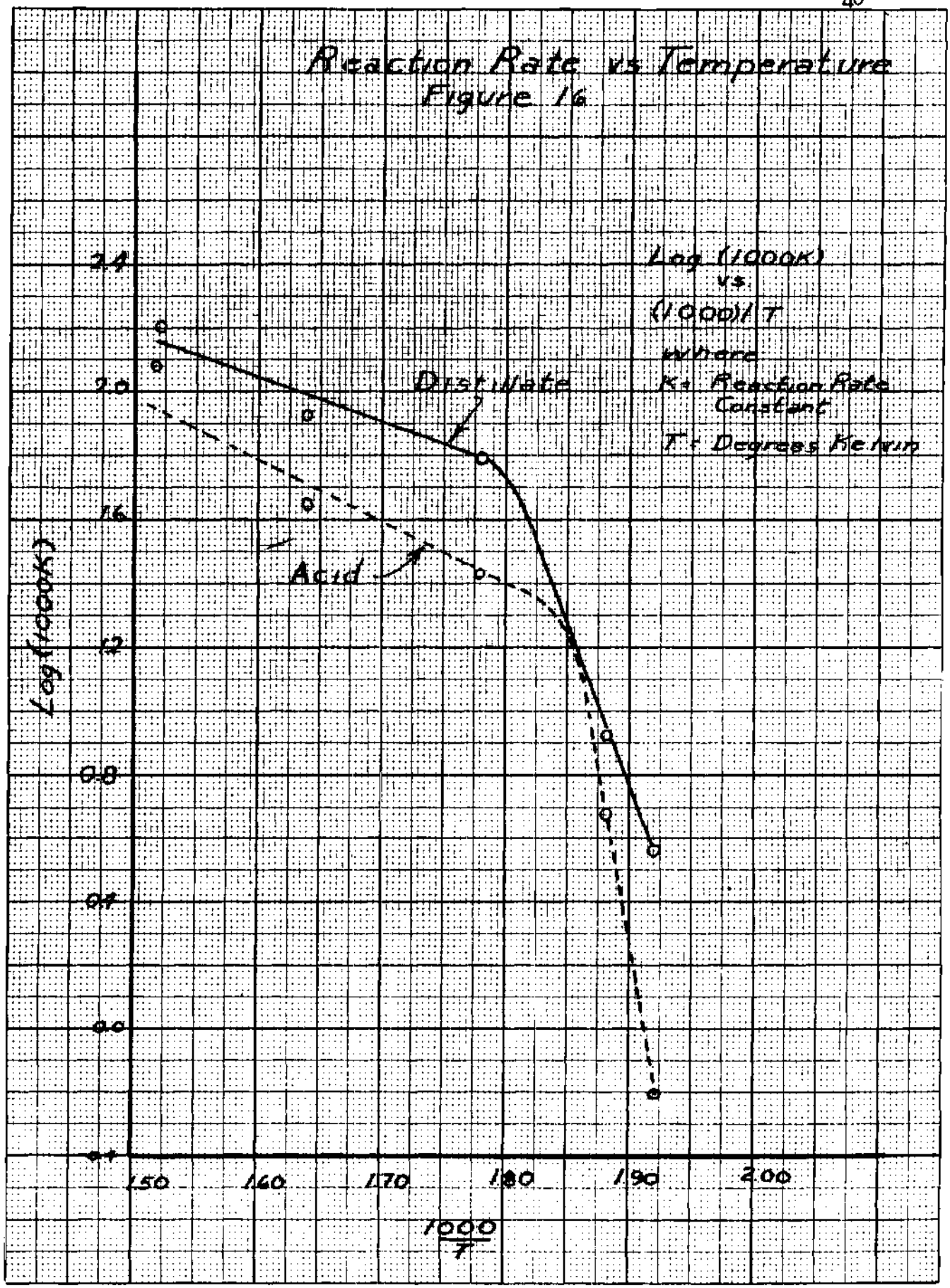

Acid Reaction
Run E-1
Temperature - 305°C
Rate of Change of
Yield vs. Average
Yield
A∞ = 2410 m.e
Figure 13
60
50
40
30
20
10
0
ΔA/Δθ
200
400
600
800
1000
1200
1400
A average

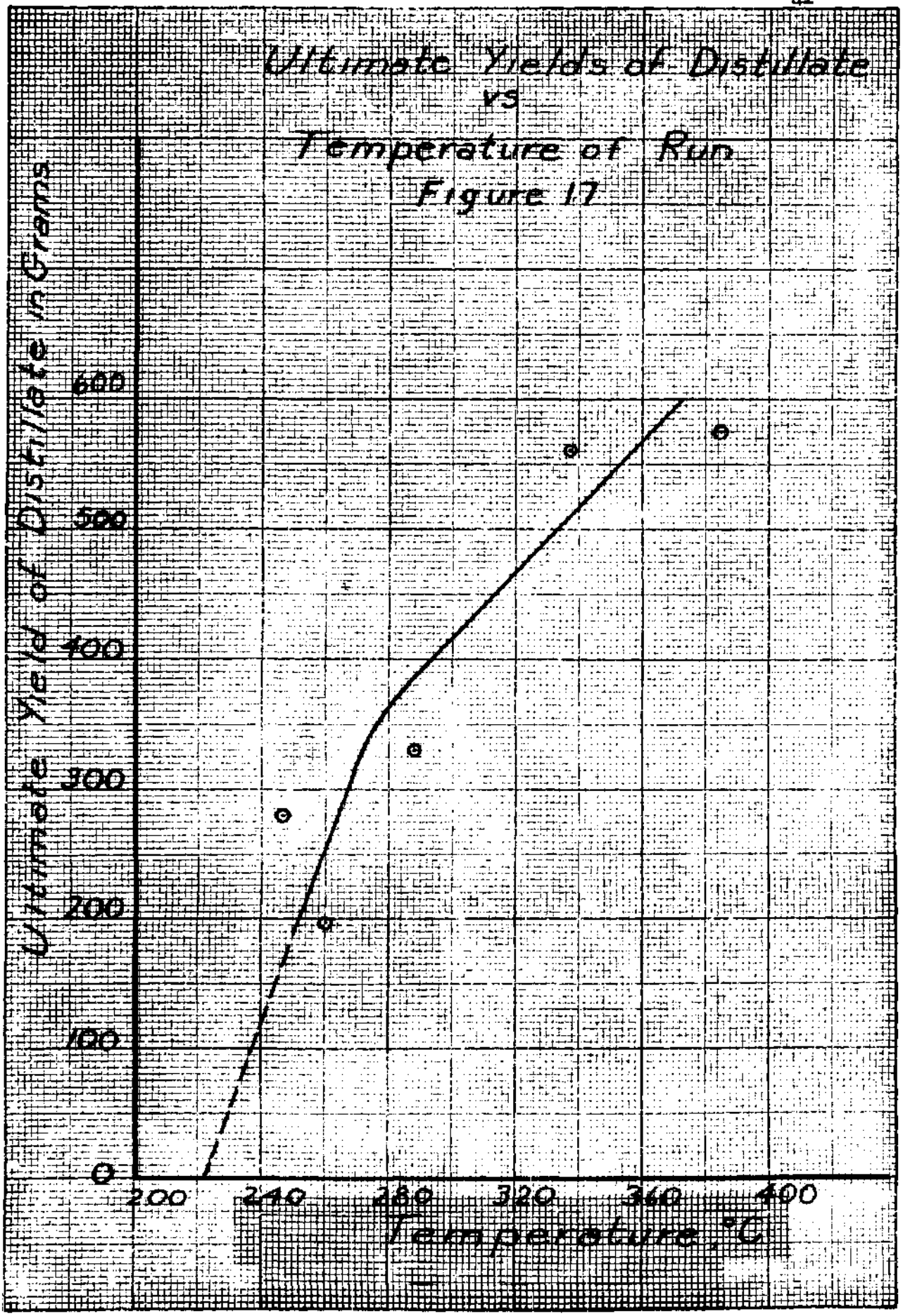

Methanol Reaction
Run B-2
Rate of Change of
Methanol Yield vs
Average Yield
Temperature - 288°C
Figure 14
0.15
0.14
0.13
0.12
0.11
0.10
ΔM/Δθ
0
2
4
6
8
10
12
M average

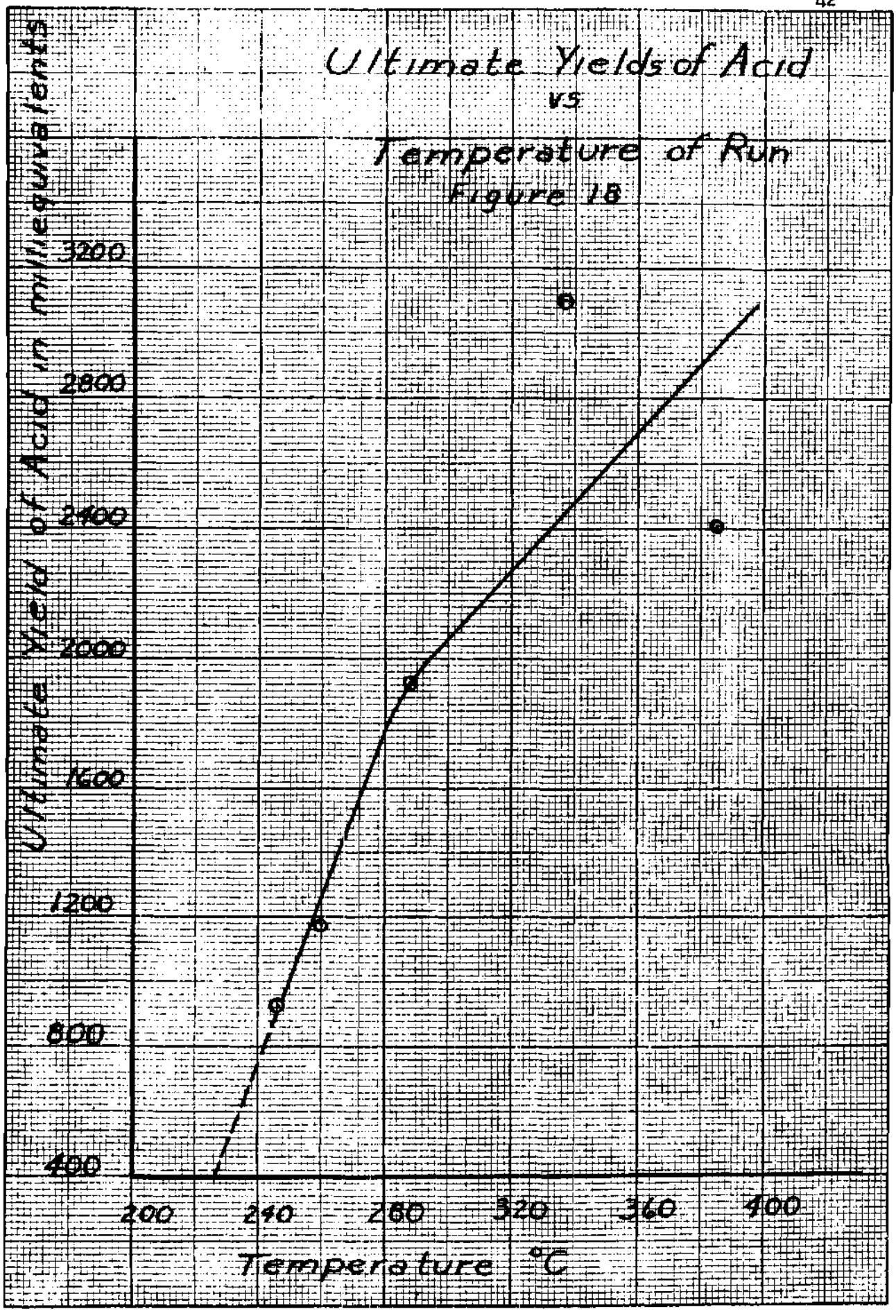

Methanol Reaction
Run D-1
Temperature 337°C.
Rate of Change of
Methanol Yield vs
Average Yield
Figure 15
0.6
ΔM/Δθ
0.5
0.4
0.3
0.2
0
5
10
15
20
25
30
35
40
M average

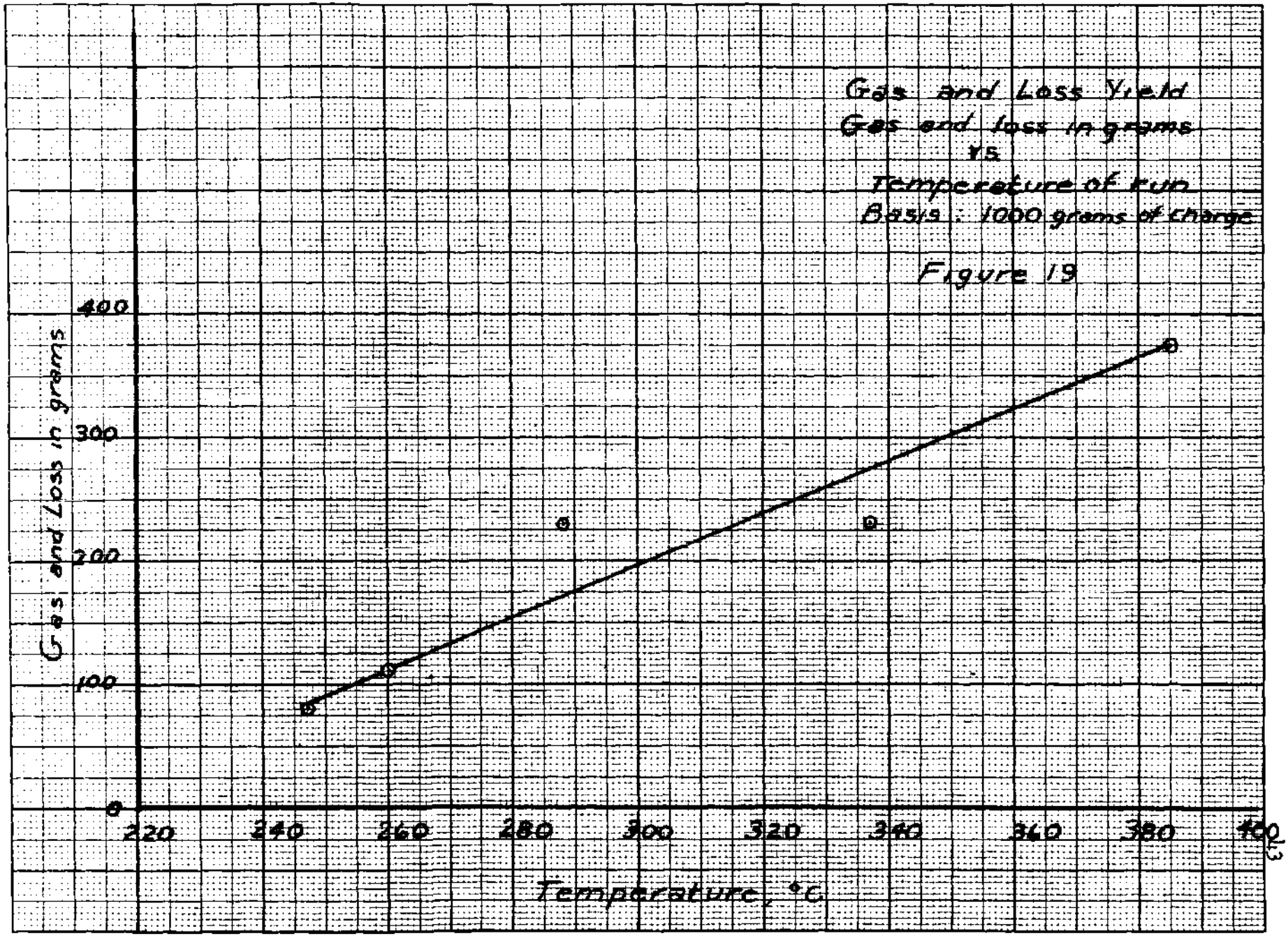
# Reaction Rate vs Temperature

Figure 16




Ultimate Yields of Distillate
vs
Temperature of Run
Figure 17
Ultimate Yield of Distillate in Grams
0
100
200
300
400
500
600
200
240
280
320
360
400
Temperature °C


Ultimate Yields of Acid
vs
Temperature of Run
Figure 18
Ultimate Yield of Acid in milliequivalents
3200
2800
2400
2000
1600
1200
800
400
200
240
280
320
360
400
Temperature °C


Gas and Loss Yield
Gas and loss in grams
vs.
Temperature of run
Basis: 1000 grams of charge
Figure 19
Gas and Loss in grams
400
300
200
100
0
220
240
260
280
300
320
340
360
380
400
Temperature, °C

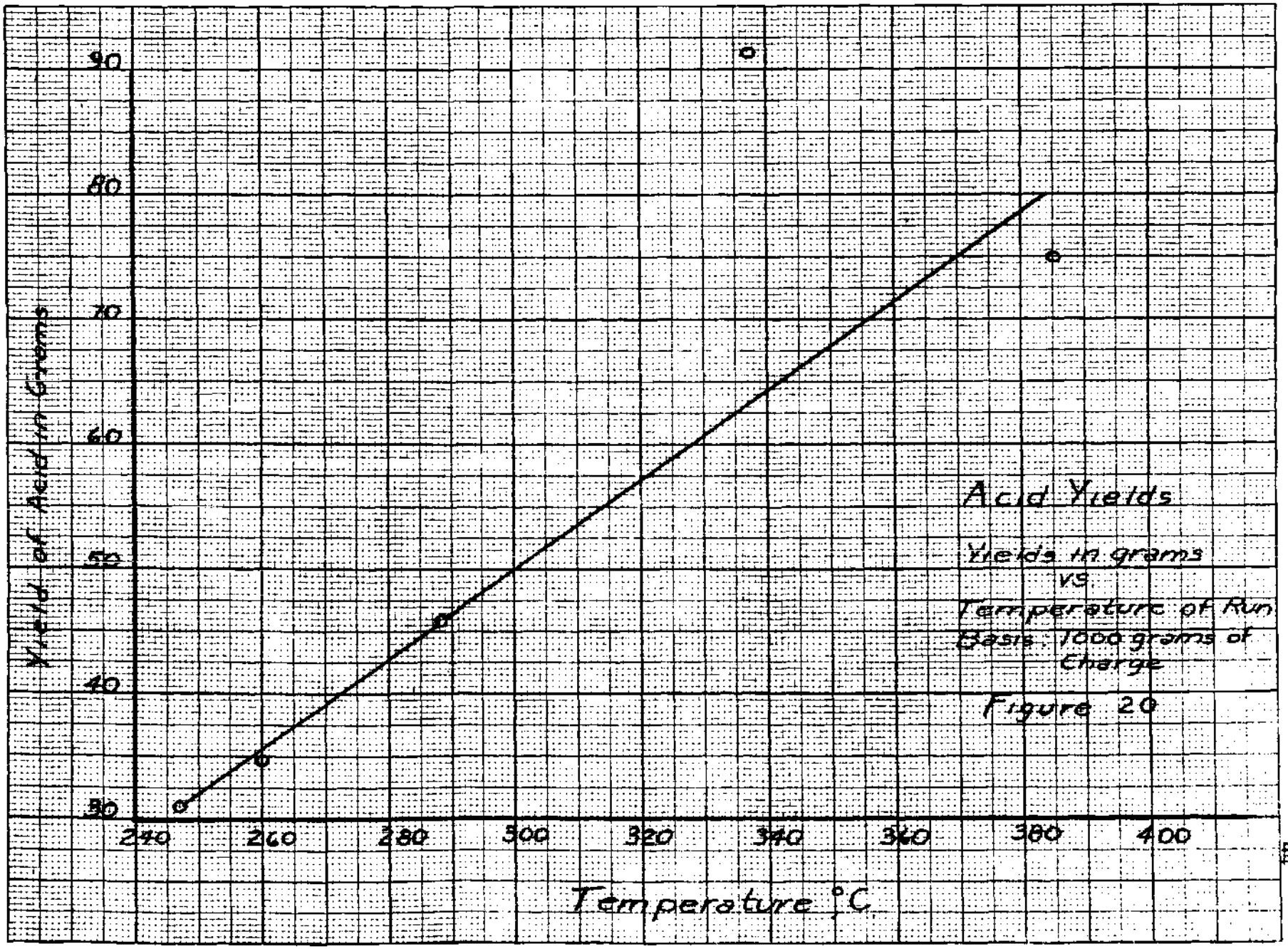
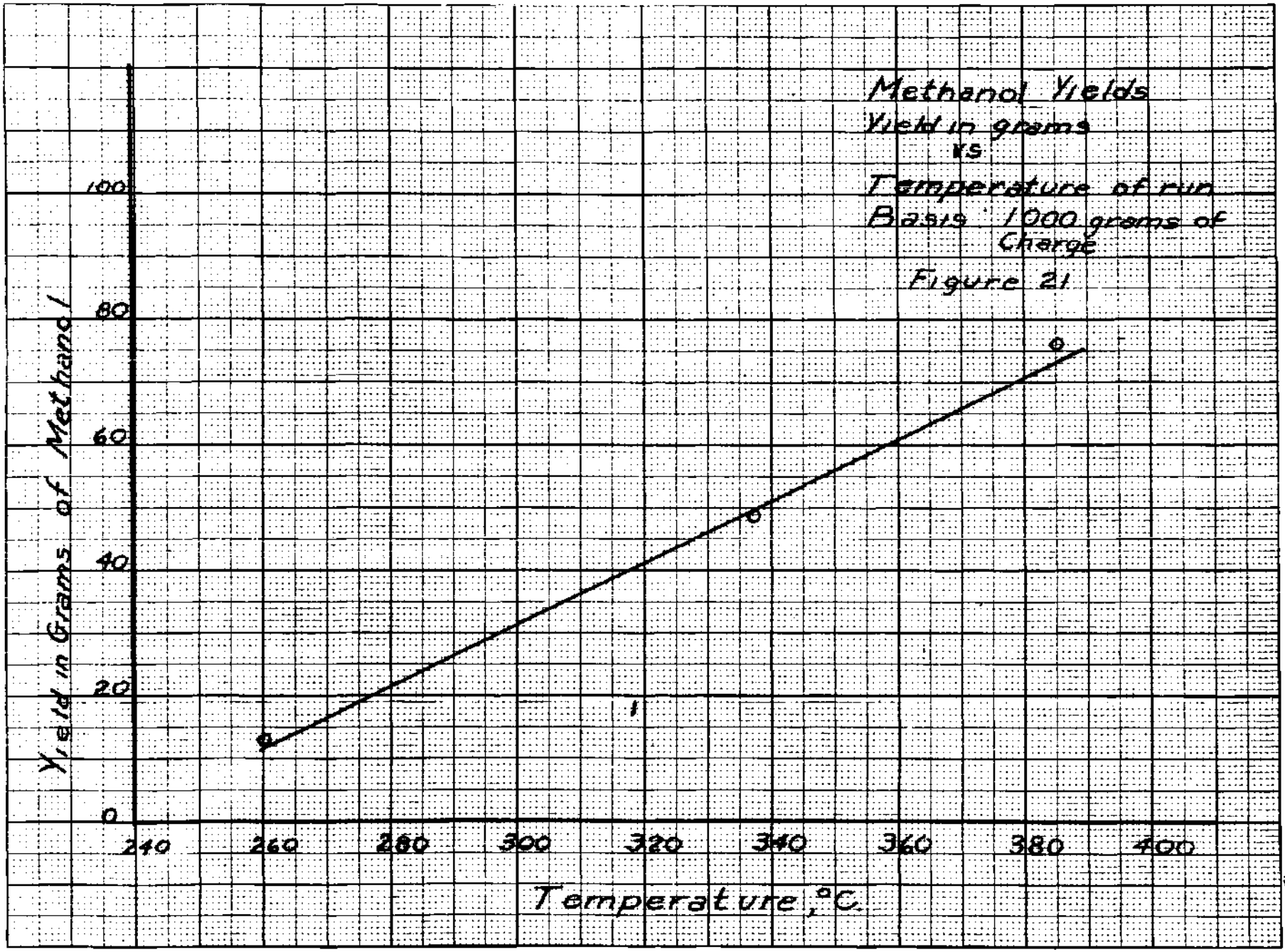
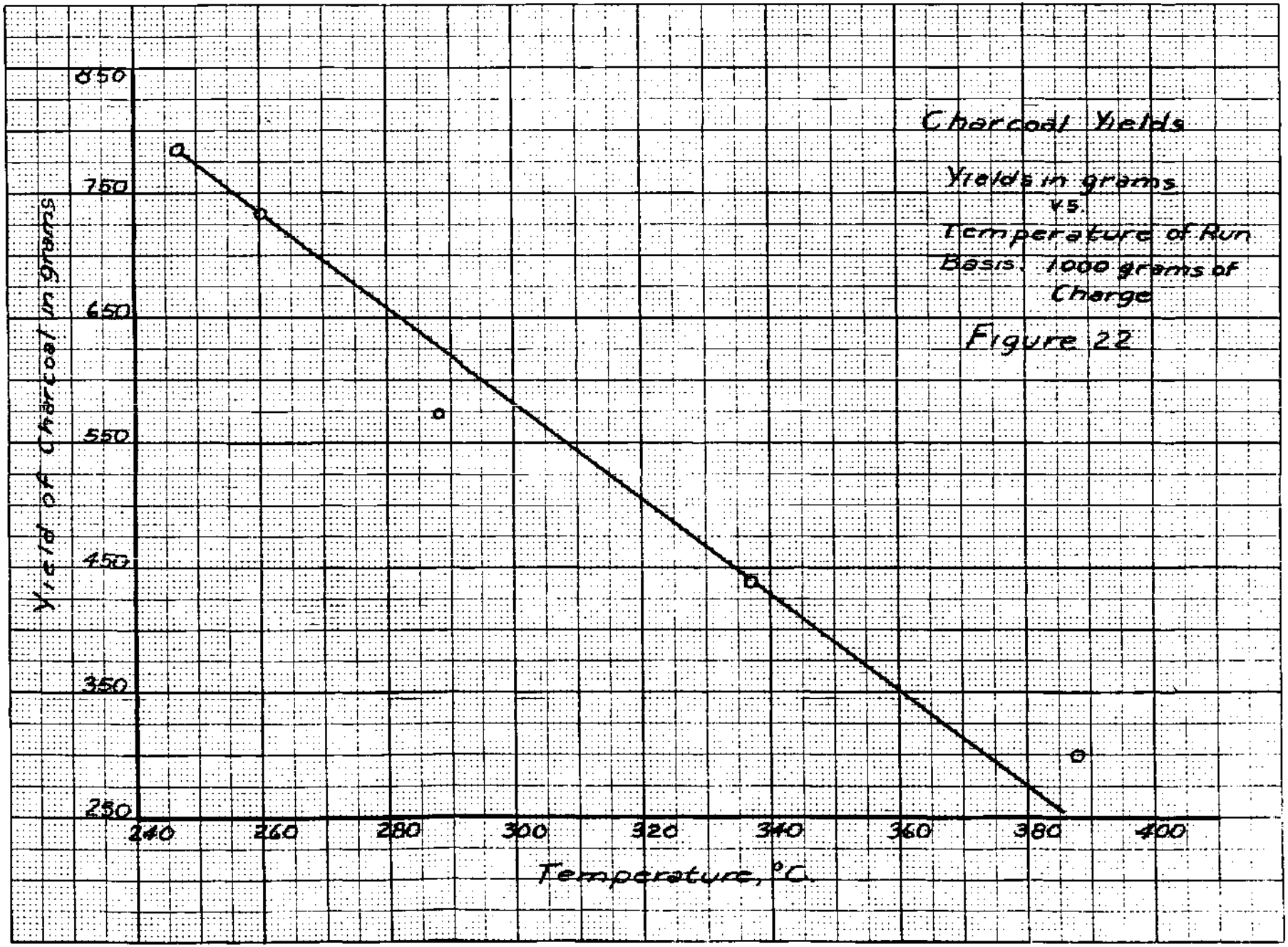

90
80
70
60
50
40
30
Yield of Acid in Grams
240
260
280
300
320
340
360
380
400
Temperature °C
Acid Yields
Yields in grams
vs
Temperature of Run
Basis 1000 grams of
Charge

Figure 20


Methanol Yields
Yield in grams
vs
Temperature of run
Basis 1000 grams of
Charge
Figure 21
Yield in Grams of Methanol
100
80
60
40
20
0
240
260
280
300
320
340
360
380
400
Temperature, °C.


Charcoal Yields
Yields in grams
vs.
Temperature of Run
Basis: 1000 grams of
Charge
Figure 22
Yield of Charcoal in Grams
850
750
650
550
450
350
250
240
260
280
300
320
340
360
380
400
Temperature, °C.

## Discussion of Results

The yields from this investigation, expressed as weight yields on a basis of air dried wood, compared favorably with those obtained in industry and reported in the scientific literature. Merrit and White (6) reported yields of 6.82% total acid and 2.25% methanol in the partial pyrolysis of red oak with steam, under laboratory conditions. The temperatures ranged from 270 to 400 degrees centigrade in their experiments. These investigators reported a yield of 4.70% acid and 2.20% methanol for a commercial distillation of red oak wood. In the present investigation, run E-1 was made at a temperature of 385 degrees centigrade. The yields for this run were 7.54% acid and 7.62% methanol. The methanol yield seemed high, but the method of analysis used was utilized previously by Othmer (3). A partial explanation of this high figure might be the presence of low molecular weight compounds which would have vaporized along with the methanol. This possibility was suggested by Othmer in his report. In addition to this, a considerable chance for error in the computation of the methanol yield lay in the fact that most of the methanol produced was carried out as vapor in the gases leaving the condenser. The amount of methanol had to be calculated from the analysis of the liquid distillate, the partial pressure of methanol over aqueous solutions, and the measured flow of gas leaving the condenser.

There were no data available in the literature on the partial pressure of methanol over pyroligneous acid solutions. From figure 26, a plot of the log of the partial pressures of methanol over water solu-

tions of varying concentrations at temperatures of 25 degrees centigrade (11), 39.9 degrees centigrade (12), and 54.9 degrees centigrade (13) versus the mole fraction of methanol in the liquid phase, it was possible to cross plot to obtain curves of partial pressure versus temperature at constant composition (figure 27). It was then necessary to extrapolate these curves to 10 degrees centigrade, the lowest temperature reached by the condenser. Similarly the partial pressure of acetic acid over pyroligneous acid solutions has not been reported. The total partial pressure of acetic acid and water for a 19.95% acetic acid solution over a wide range of temperatures was reported (14). Since this concentration was very close to the average concentration of acid in the distillate, these values were utilized for the determination of the partial pressures. The partial pressure of the water was calculated by applying Raoult's law.

No data on charcoal and distillate yields from the destructive distillation of red oak were available. The yields from fluidized distillation at 385 degrees centigrade, which were 30.9% charcoal and 32.5% distillate, may be compared with values of 31.8% and 43.9%, respectively, for birch, a typical hardwood (15).

Generally speaking, the operation of the apparatus was satisfactory. Some difficulty was experienced in Run B-2 due to the clogging of the exit line from the reactor to the cyclone separator. Closing of the pressure taps in the reactor by sawdust was frequent, in spite of a small flow of nitrogen through them. There was a tendency for liquid to condense in the cyclone separator and the line leading to the separator from the reactor. Sawdust and tar blocked the slide valves above and below

the reactor during two runs, but these were not serious. When the cold sawdust charge was introduced into the hot reactor, a drop in temperature of approximately 70 degrees centigrade was immediately noted. Some allowance for this drop was always necessary in determining the temperature at which the run was to be made. The Orsat apparatus developed leaks frequently and caused delays in the analysis of gas samples. The cyclone separator worked well, and only in one case was there any evidence of sawdust particles in the condenser. After Run B-2 the top of the apparatus was removed along with the condenser and the separator, and the equipment was checked for corrosion. Some tar was deposited in the separator, but there was none in the condenser. No evidence of corrosion was found in any of the articles examined.

The two most serious defects in design were the inadequacy of the condensation system and the heat losses from the top and bottom of the reactor. The exit gas leaving the condenser swept out vapors of methanol, acid and water present over the distillate collected in the condenser. Cooling water was never able to reduce the condenser temperature below 12 degrees centigrade even during the winter. The uninsulated metal masses at the top and bottom of the reactor were continually losing heat to the surroundings. This heat loss caused the thermocouples at the ends of the reactor to be continually lower than the center thermocouple, number two. Since this lower temperature area was small in comparison with the total area of the reactor, number two thermocouple at the center of the reactor was chosen as indicating the temperature of the charge being distilled. Readings were taken of all thermocouples, however.

The order of the destructive distillation reaction was found to change rapidly from first order to a higher order reaction in the vicinity of the exothermic stage. Figures 4, 5, 9, and 10 showed that for both acid and distillate the rate of change of yield versus average yield was a straight line variation, indicating a first order reaction. This was true for both the 247 degree centigrade run and the 260 degree centigrade run. This region corresponded to the stage of low temperature partial decomposition noted by previous investigators (4) and extended almost to the temperature at which the exothermic decomposition stage occurs. Above this temperature the reaction changed into a higher order reaction for both the acid and the distillate. (See figures 6, 7, 8, 11, 12, and 13). The fact that the amount of data on methanol was relatively small prevented any clear cut analysis of the order of the reaction. In the exothermic region, attempts to correlate the data on the basis of a second order reaction were unsuccessful, and it was evident that the order of the reaction was probably somewhat higher than second. It was considered that the precision of the data was not such as to justify the involved calculations necessary to investigate higher orders. In order to have some idea as to the order of magnitude of the reaction rate constant, for the high order reaction, the approximate slope of the left hand section of the curves was taken. In each case, the greater portion of the reaction took place in the region of the curve; and hence this step seemed justified. The rate constants obtained were tabulated for the acid, and the distillate curves at each of the temperatures of the five runs. The logs of these rate constants were then plotted against the reciprocal of the temperatures at which the constants were obtained.

The rate constants above and below the exothermic stage for both the acid and the distillate showed a significant similarity, both in magnitude and in the effect of temperature. (See figure 16). In the region below the temperature at which the exothermic decomposition begins, a small increase in temperature caused a large increase in the rate constant, indicating a high temperature coefficient for the reaction in this region. This high temperature coefficient is typical of first order reactions, in many of which a 10 degree centigrade temperature rise causes the reaction rate to double. It also indicates that a thermal decomposition is occurring as the predominant reaction. The upper region shows a low temperature coefficient, a large increase in temperature producing a small increase in reaction rate. The low temperature coefficient reactions are, as a general rule, the polymerization and condensation types of reactions. In this case, there may be condensation of cellulose rings to form condensed cyclic compounds or phenolic tars.

The rate constants for acid and distillate are of the same order of magnitude in approximately the same region. This would seem to indicate some sort of relation between the formation of the distillate and the acid, in that they may both be derived from the same source.

The existence of two regions with regard to reaction order was also suggested by the plots of ultimate yields at infinite time for acid and distillate against temperature. (See figures 17 and 18) Figure 18 indicated a slight break in the curve in the neighborhood of 280 degrees centigrade. Extrapolation of the lower part of the curve in figure 18 to

zero yield showed that production of acid was probably negligible below about 230 degrees centigrade. On the assumption that the ultimate yield of distillate was also negligible at 230 degrees centigrade (except for free moisture), the lines on figure 17 were then drawn. The results indicated the probability of a break in the curve on figure 17, similar to that on figure 18.

Thus, a change in the order of magnitude, of the ultimate yields, a change in the order of reaction at constant temperature, and a change in the temperature coefficient of reaction all appeared to occur in the neighborhood of 280 degrees centigrade. The inference that a basic change in the reaction mechanism takes place in the neighborhood of 280 degrees centigrade was hard to avoid.

## Conclusions

1. The destructive distillation of sawdust in a fluidized system appears to be practical, from the point of view of operability. Difficulties due to agglomeration of particles were not experienced.
2. The yields of products by distillation in a fluidized system are comparable with those reported for the conventional processes of wood distillation. The methanol yields may be higher than those previously noted, but evidence on this point is not firm.
3. The reaction rates obtainable in a fluidized bed are much greater than those reported for the conventional processes of wood distillation. Thus, at 385 degrees centigrade 70% of the wood was gasified in less than two hours.
4. The design and equipment utilized in this investigation were satisfactory with regard to their operation, with one or two minor exceptions.
5. The destructive distillation reaction appears to be a first order reaction below about 280 degrees centigrade and of a higher order above this temperature. This is true for both acid formation and distillate formation.
6. The change in order of reaction occurs at almost the same point, indicating some relation between the acid and distillate formation.
7. The rate constants of both the acid and distillate reactions are of the same order of magnitude, further emphasizing the existence of some relation between the formation of the two products.

8. The rate constants for both acid and distillate formation exhibit a high temperature coefficient in the lower decomposition region indicating that a decomposition type reaction is the controlling factor in determining the rate of production of acid and water.
9. The rate constants in the supper, or exothermic, range show a low temperature coefficient. This suggests that here a polymerization or condensation type of reaction controls the rate of production of acid and water.
10. The data on methanol formation indicate a slower reaction rate than that of either the acid or distillate reaction.
11. The reaction to form methanol is probably second order or higher, with a low temperature coefficient.

## Recommendations

1. The accuracy of measurement of yields would be increased by a recovery system, which could remove the vapors in the exit gas stream. The use of adsorption, or alternatively, absorption with a suitable solvent would serve to remove the acid and methanol vapors from the exit gas stream.

2. The installation of an electrical heating circuit would decrease the heat losses from the ends of the reactor. This would serve to make the operation more nearly isothermal during distillation runs.

3. Preheating of the incoming fluidizing gas prior to its entry into the reactor would decrease the temperature drop when the charge of sawdust is introduced and would also aid in maintaining isothermal conditions within the reactor throughout the progress of a run.

4. Installation of an auxiliary gas flow system to keep the pressure taps open and free of sawdust during a distillation run would increase the efficiency of the apparatus.

5. The flow meters now installed should be replaced with meters which would give larger manometer readings. The exit gas stream should have a low flow rate meter and a bypass connection to a high flow rate meter, in order that the extreme variations of flow could be accurately measured.

6. A larger line, at least $1\frac{1}{2}$ inch diameter pipe, should be substituted for the present connection between the reactor and the cyclone separa-

tor.

7. The tendency for liquid to condense in the cyclone separator could be corrected by a larger heating element and by better insulation of the cyclone separator.

8. To prevent the accumulation of tars within the disengaging section and the cyclone separator, the present set up should be modified to permit examination and cleaning of these sections.

9. The gas analysis in future runs should be made more frequently. A new Orsat apparatus, free of leaks, is needed. It would be deniable to use a setup equipped for analysis for hydrogen, methane, and olefins, as well as carbon dioxide and carbon monoxide.

10. The construction of a small scale fractionating column for a complete distillation analysis of liquid products is suggested.

11. This investigation should be extended to study the effect of particle size and other process variables on the operating characteristics of this design and on the yields of products.

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# APPENDIX

## Sample Calculations

I. Calculation of meter constants from calibration data

Gram moles per hour is equivalent to

$$\frac{(\text{Cubic feet per second})(\text{Seconds per hour})(\text{liters per cubic foot})}{(\text{liters per gram mole})}$$

$$\frac{(\text{Cubic feet per second})(3600)(28.32)}{(22.41)}\frac{(273)}{T}$$

(1) $$\frac{(1{,}240{,}000)(\text{Cubic feet per second})}{(\text{Temperature of Calibration})}$$

From Bernoullis Theorem it can be shown that

Gram moles are equivalent to

(2) $$(K)\sqrt{\frac{MWc}{MWg}\ \frac{P}{Pc}\ \frac{Tc}{T}\ \Delta P}$$

Where:

| | |
|---|---|
| MWc | is the molecular weight of the calibrating gas |
| MW | is the molecular weight of gas being measured |
| Pc | is static pressure at calibration |
| P | is static pressure at measurement |
| Tc | is gas temperature at calibration |
| T | is gas temperature at measurement |
| P | is manometer reading |
| K | is the meter constant |

At the calibration of the three meters used in this work the temperatures were as follows:

Orifice Meter One - 21 degrees centigrade

Orifice Meter Two - 21 degrees centigrade

Capillary Meter - 20 degrees centigrade

The pressure in all cases was substantially atmospheric.

During calibration runs equation 2 reduced to

Gram moles are equal to $K\sqrt{\Delta P}$

Combining equation 2 with equation 1

(3) K is equal to $\frac{(1,240,000)\ (\text{Cubic feet per second})}{(Tc)\ \sqrt{\Delta P}}$

Example:

For orifice meter one

Tc was 21 degrees centigrade

Equation 3 reduced to:

$$K = \frac{(4240)\ (\text{Cu.ft. per sec.})}{\sqrt{\Delta P}}$$

| | | | |
|---|---|---|---|
| $\Delta$ P - 2.0 | Cu.ft./sec. - | .0105 | K = 31.55 |
| $\Delta$ P - 3.0 | Cu.ft./sec. - | .0129 | K = 31.60 |
| $\Delta$ P - 9.0 | Cu.ft./sec. - | .0230 | K = 31.50 |
| $\Delta$ P - 1.0 | Cu.ft./sec. - | .0074 | K = 31.40 |

K average - 31.51= 31.5

For orifice meter two

Average K was 35.0

For capillary meter

Average K was 15.0

II. Determination of Water Vapor, Methanol and Acid, Calculated as acetic, in Exit Gas Stream.

Example: Run D-1 Time - 60 minutes

Data: Inlet meter pressure drop - 2.0 cm

Exit meter pressure drop - 10.8 cm

Average inlet gas temperature - 24 degrees centigrade

Average condenser temperature - 20 degrees centigrade

Average molecular weight of exit gas - 28.5

Mole percent methanol indistillate - 4.98

Average weight percent acetic acid in distillate - 20.61%

Vapor pressure pure water at 20 degrees centigrade - 17.35 m.m. of Hg.

Nitrogen entering - $31.5 \sqrt{\frac{294}{297}\ (2)}$

- 44.3 Gm. mols per hour

Partial pressure of acetic acid and water mixture at 20 degreen centigrade (Fig. 25) - 16.9 mm. of hg.

Assuming Raoult's Law, partial pressure of water - (.7939)(.1735) or 13.8 m.m.

Partial pressure of acid - 3.1 m.m.

Partial pressure of methanol (Fig. 27) - 5.02 m.m.

Exit gas from meter reading

$$15.0 \sqrt{\frac{28}{MW}\ 10.8}$$

$$15.0\sqrt{\frac{28}{28.5}\quad 10.8}$$

48.8 gm. mols per hour

Assuming total pressure of 760 m.m.

Water vapor in exit stream is:

$\frac{13.8}{760}$ (48.8) or 0.199 Gm. mols per hour

Methanol in exit stream

$\frac{5.02}{760}$ (48.8) or 0.322 gm. mols per hour

Total moles vapor in exit stream - 1.407

Total moles gas other than nitrogen - 3.09

## Explanation of Headings for Tables

I, II, III, IV and V

A. Temperature of thermocouple 1 in centigrade degrees

B. Temperature of thermocouple 2 in centigrade degrees

C. Temperature of thermocouple 3 in centigrade degrees

D. Temperature of thermocouple 4 in centigrade degrees

E. Temperature of condenser in centigrade degrees

F. Temperature of inlet gas in centigrade degrees

G. Reading of orifice meter No. 1 manometer in centimeters of ethylene dibromide

H. Static pressure at bottom of reactor in centimeters of ethylene dibromide

I. Reading of orifice meter No. 2 manometer in centimeters of ethylene dibromide

J. Pressure drop through fluidized bed in centimeters of Mercury

K. Number of gas sample

L. Number of liquid sample

M. Static pressure at the bottom of reactor in millimeters of mercury

N. Reading on manometer reading of capillary meter in centimeter of acetylene tetra bromide

Table I
Original Data
Run C-2

| Time Mins. | A | B | C | D | E | F | G | N | J | L | K | Time Gas Sample |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | | | | | | | | 0 |
| 1 | 110 | 248 | 201 | 160 | | | 2.0 | | | | 1 | 5 |
| 3 | 117 | 248 | 205 | 162 | | | | 10.0 | 1.38 | 1 | 2 | 9 |
| 4 | | | | | | | | 10.0 | 1.38 | | 3 | 15 |
| 6 | 146 | 246 | 207 | 163 | | | | | | | 4 | 25 |
| 8 | | | | | 17 | 21 | | 10.0 | 1.29 | 2 | 5 | 29 |
| 10 | 154 | 246 | 208 | 167 | | | | 9.2 | 1.25 | | 6 | 35 |
| 13 | 164 | 248 | 214 | 170 | 17 | 21 | 2.0 | 10.0 | 1.29 | 3 | 7 | 145 |
| 18 | 170 | 247 | 216 | 172 | | | | 9.2 | 1.25 | 4 | | |
| 23 | 173 | 248 | 217 | 172 | | | | 10.0 | 1.25 | 5 | | |
| 28 | 176 | 246 | 218 | 173 | 17 | 21 | | 8.6 | 1.25 | 6 | | |
| 33 | 180 | 247 | 219 | 174 | | | | 10.0 | 1.21 | 7 | | |
| 38 | 184 | 245 | 219 | 175 | | | | 10.0 | 1.16 | | | |
| 43 | 184 | 246 | 224 | 177 | 17 | 21 | 2.0 | 9.2 | 1.16 | 8 | | |
| 48 | 190 | 247 | 226 | 178 | | | | 9.2 | 1.12 | | | |
| 53 | 189 | 246 | 226 | 179 | | | | 10.0 | 1.12 | 9 | | |
| 58 | 192 | 245 | 228 | 180 | | | | 10.0 | 1.08 | | | |
| 63 | 194 | 247 | 230 | 182 | 17 | 21 | 2.0 | 9.2 | 1.08 | 10 | | |
| 68 | 193 | 246 | 230 | 182 | | | | | | | | |
| 73 | 194 | 244 | 232 | 184 | | | | 9.2 | 1.08 | 11 | | |
| 83 | 197 | 247 | 235 | 185 | | | 2.0 | 10.0 | 1.08 | 12 | | |
| 88 | 198 | 247 | 237 | 189 | | | | 9.2 | 1.08 | | | |
| 93 | 200 | 247 | 237 | 189 | 17 | 21 | | | | 13 | | |
| 98 | 200 | 246 | 237 | 190 | | | | 9.2 | 1.03 | | | |
| 103 | 199 | 247 | 238 | 190 | | | | 8.6 | 1.08 | 14 | | |
| 108 | 199 | 247 | 239 | 192 | | | | 8.6 | 1.03 | | | |
| 113 | 200 | 247 | 241 | 193 | | | | 8.6 | 1.03 | 15 | | |
| 118 | 200 | 249 | 242 | 194 | 17 | 21 | 2.0 | 9.2 | 1.03 | | | |
| 123 | 200 | 247 | 241 | 193 | 17 | 21 | 2.0 | 8.6 | 1.03 | 16 | | |
| 128 | 200 | 247 | 241 | 194 | 17 | 21 | 2.0 | 9.2 | 0.99 | | | |
| 133 | 199 | 247 | 241 | 193 | | | | 8.6 | 0.99 | 17 | | |
| 138 | 199 | 247 | 241 | 194 | 17 | 21 | | 8.6 | 0.99 | | | |
| 143 | 200 | 247 | 241 | 192 | | | 2.0 | 8.6 | 0.99 | 18 | | |
| Avg. | 181 | 247 | 228 | 181 | 17 | 21 | 2.0 | 9.3 | | | | |

Table II
Original Data
Run A-4

| Time Mins. | A | B | C | D | E | F | G | H | I | J | K | L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 144 | 334 | 206 | 160 | | | | | | | | |
| 2 | 147 | 276 | 208 | 185 | | | | | | | | |
| 3 | 154 | 276 | 214 | 201 | | | 2.0 | 9.8 | 1.6 | 1.42 | | |
| 8 | 164 | 261 | 226 | 200 | 13 | 22 | 2.0 | | 1.6 | 1.33 | 1 | |
| 12 | 168 | 257 | 224 | 198 | | | | | | | | |
| 13 | 172 | 257 | 226 | 196 | | | | 9.6 | 1.6 | 1.33 | | |
| 16 | | | | | | | | | | | 2 | 1 |
| 21 | 177 | 256 | 226 | 194 | | | | | | | | |
| 23 | | | | | | | | | | | | 2 |
| 25 | | | | | | | 2.0 | 9.6 | 1.6 | 1.29 | 3 | |
| 28 | 178 | 257 | 223 | 192 | | | | | | | | |
| 30 | | | | | | | 2.0 | 9.2 | 1.5 | 1.20 | | 3 |
| 33 | 179 | 257 | 223 | 192 | 11 | 21 | | | | | | |
| 38 | 184 | 258 | 226 | 192 | | | | 9.2 | 1.6 | 1.20 | | |
| 40 | | | | | | | | | | | | 4 |
| 43 | 186 | 260 | 226 | 194 | 11 | 21 | 2.0 | 9.8 | 1.6 | 0.82 | | |
| 48 | 185 | 261 | 225 | 191 | | | 2.0 | | | | | |
| 53 | 185 | 257 | 223 | 190 | | | 2.0 | | | | 4 | 5 |
| 58 | 186 | 258 | 226 | 190 | 11 | 21 | 2.0 | | 1.6 | 0.82 | | |
| 63 | 188 | 264 | 227 | 191 | | | 2.0 | 10.2 | 1.6 | 0.73 | | |
| 68 | 187 | 260 | 225 | 190 | | | 2.0 | 10.6 | 1.6 | 0.69 | | 6 |
| 73 | 186 | 260 | 225 | 188 | | | 2.0 | 10.6 | 1.5 | 0.69 | | |
| 83 | 187 | 259 | 225 | 190 | | | 2.0 | 10.6 | 1.6 | 0.69 | 5 | 7 |
| 88 | 189 | 259 | 225 | 190 | 11 | 21 | 2.0 | 10.6 | 1.7 | 0.65 | | |
| 98 | 189 | 259 | 225 | 190 | 11 | 22 | 2.0 | 10.6 | 1.7 | 0.65 | | 8 |
| 108 | 189 | 259 | 227 | 191 | | | 2.0 | 11.0 | 1.7 | 0.60 | | |
| 113 | | | | | | | | | | | | 9 |
| 118 | 189 | 260 | 228 | 191 | | | 2.0 | 11.0 | 1.7 | 0.60 | | |
| 123 | 187 | 258 | 228 | 191 | | | | | | | | |
| 128 | 187 | 259 | 228 | 191 | | | 2.0 | | | | | 10 |
| 138 | 189 | 260 | 232 | 195 | | | 2.0 | 11.2 | 1.7 | 0.60 | | |
| 143 | 189 | 260 | 231 | 194 | | | 2.0 | 11.0 | 1.7 | 0.56 | | 11 |
| 153 | 188 | 260 | 231 | 194 | | | 2.0 | 11.0 | 1.7 | 0.56 | | |
| 158 | 188 | 260 | 231 | 196 | 11 | 22 | 2.0 | 10.6 | 1.7 | | | 12 |
| 168 | 188 | 261 | 234 | 196 | | | 2.0 | 9.8 | 1.9 | 0.56 | | |
| 173 | 187 | 259 | 230 | 196 | | | 2.0 | 9.8 | 1.9 | 0.60 | | 13 |
| 188 | 185 | 254 | 231 | 196 | 11 | 22 | 2.0 | 10.6 | 1.9 | 0.60 | 6 | 14 |
| Avg. | 182 | 260 | 226 | 193 | 11 | 21.5 | 2.0 | | 1.7 | | | |

Table III
Original Data
Run B-2

| Time Mins. | A | B | C | D | E | F | G | M | I | J | K | L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 145 | 293 | 249 | 212 | | | | | | | | |
| 1 | 198 | 296 | 254 | 217 | | | 2.0 | 1.6 | 1.7 | 1.19 | | |
| 4 | | | | | | | 2.0 | 1.6 | 1.7 | 1.13 | | |
| 6 | | | | | 12 | 21 | | | | | | 1 |
| 9 | | | | | | | 2.0 | 1.6 | 1.7 | 1.09 | | |
| 10 | 229 | 289 | 257 | 222 | 12 | 20 | | | | | | 2 |
| 12 | 229 | 289 | 257 | 222 | | | | | | | | |
| 14 | 237 | 290 | 259 | 220 | | | 2.0 | 1.6 | 1.7 | 1.13 | | |
| 15 | | | | | | | | | | | | 3 |
| 18 | | | | | | | 2.0 | 1.6 | 1.9 | 1.09 | | |
| 20 | | | | | 12 | 20 | | | | | 1 | 4 |
| 22 | | | | | | | 2.0 | 1.6 | 1.9 | 1.01 | | |
| 25 | 245 | 290 | 266 | 225 | 12 | 20 | | | | | | 5 |
| 28 | | | | | | | 2.0 | 1.6 | 1.7 | 0.92 | | |
| 30 | 247 | 288 | 265 | 229 | 12 | 20 | | | | | | 6 |
| 35 | 246 | 287 | 266 | 228 | | | | | | | | |
| 37 | | | | | | | 2.0 | 1.4 | 1.6 | 0.83 | | |
| 39 | 247 | 288 | 268 | 231 | | | | | | | | |
| 40 | 247 | 288 | 268 | 231 | 12 | 20 | 2.0 | 1.2 | 1.9 | 0.92 | | 7 |
| 49 | 249 | 288 | 270 | 232 | | | | | | | 2 | 8 |
| 53 | | | | | | | 2.0 | 1.3 | 1.5 | 0.96 | | |
| 54 | 245 | 288 | 269 | 235 | | | | | | | | |
| 58 | | | | | | | 2.0 | 1.1 | 1.7 | 0.92 | | |
| 59 | 244 | 285 | 269 | 235 | | | | | 1.9 | | | 9 |
| 61 | | | | | 12 | 20 | 2.0 | 1.0 | 1.9 | 0.92 | | |
| 64 | 246 | 286 | 272 | 238 | | | | | | | | |
| 69 | 249 | 290 | 277 | 241 | | | | | | | | 10 |
| 79 | 241 | 283 | 274 | 244 | | | | | | | 3 | 11 |
| 84 | 243 | 285 | 278 | 245 | | | | | | | | |
| 89 | 241 | 287 | 279 | 246 | | | | | | | | 12 |
| 99 | 240 | 287 | 280 | 249 | 12 | 20 | 2.0 | 1.0 | 1.7 | 0.83 | 4 | 13 |
| 109 | 236 | 286 | 283 | 249 | | | | | | | | 14 |
| 114 | 234 | 288 | 284 | 251 | 12 | 20 | 2.0 | 0.8 | 1.5 | | | |
| 119 | 234 | 288 | 284 | 254 | | | 2.0 | 0.8 | 1.3 | | 5 | 15 |
| Avg. | 240 | 288 | 271 | 236 | 12 | 20 | 2.0 | | 1.7 | | | |

Table IV
Original Data
Run D-1

| Time Mins. | A | B | C | D | E | F | G | N | H | J | L | K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 142 | 346 | 270 | 232 | | | | | | | | |
| 3 | 200 | 338 | 282 | 225 | | | | 27.0 | 6.4 | 105 | | |
| 5 | | | | | | | | | | | | |
| 7 | 239 | 336 | 284 | 221 | | | | | | | 1 | 1 |
| 10 | | | | | | | | | | | 2 | |
| 11 | 259 | 336 | 290 | 226 | | | | | | | | |
| 15 | 274 | 336 | 295 | 230 | | | | | | 0.92 | 3 | |
| 17 | 281 | 337 | 300 | 234 | | | | | | | | |
| 20 | 279 | 335 | 300 | 234 | 20 | 24 | 2.0 | 14.8 | 3.6 | 0.79 | 4 | |
| 23 | 278 | 335 | 300 | 236 | | | | | | | | |
| 25 | 276 | 337 | 302 | 239 | 20 | 24 | 2.0 | 12.2 | 3.6 | 0.75 | 5 | |
| 28 | 276 | 338 | 302 | 240 | | | | | | | | |
| 30 | 273 | 336 | 300 | 239 | | | 2.0 | 12.0 | 3.6 | 0.61 | 6 | 2 |
| 33 | 269 | 335 | 299 | 239 | | | | | | | | |
| 35 | 266 | 336 | 300 | 283 | | | 2.0 | 12.0 | 3.2 | 0.61 | 7 | |
| 38 | 264 | 336 | 302 | 239 | | | | | | | | |
| 40 | 262 | 337 | 301 | 238 | 20 | 24 | 2.0 | 11.8 | 3.2 | 0.56 | 8 | |
| 43 | 260 | 336 | 302 | 240 | | | | | | | | |
| 45 | 257 | 335 | 302 | 239 | | | 2.0 | 10.8 | 2.8 | 0.56 | 9 | |
| 48 | 256 | 336 | 302 | 238 | | | | | | | | |
| 50 | 254 | 337 | 302 | 239 | | | 2.0 | 10.8 | 2.8 | 0.56 | 10 | |
| 55 | 253 | 337 | 302 | 239 | 20 | 24 | | | | 0.53 | | |
| 60 | 249 | 338 | 306 | 244 | 20 | 24 | 2.0 | 10.8 | 2.8 | 0.48 | 11 | |
| 65 | 248 | 338 | 304 | 245 | 20 | 24 | 2.0 | 11.0 | 3.0 | 0.48 | | 3 |
| 70 | 243 | 336 | 304 | 245 | | | 2.0 | 10.8 | 3.0 | 0.44 | 12 | |
| 75 | 243 | 346 | 310 | 246 | | | 2.0 | 10.2 | 2.8 | 0.48 | | |
| 80 | 247 | 354 | 314 | 250 | | | 2.0 | 10.8 | 2.6 | 0.48 | 13 | |
| 85 | 241 | 346 | 312 | 252 | | | | | | | | |
| 90 | 235 | 339 | 310 | 249 | 20 | 24 | 2.0 | 11.0 | 2.8 | 0.48 | 14 | |
| 95 | 235 | 340 | 311 | 250 | | | | | | | | |
| 100 | 230 | 338 | 309 | 250 | | | 2.0 | 10.4 | 2.8 | 0.48 | 15 | |
| 105 | 222 | 336 | 308 | 249 | 20 | 24 | 2.0 | 10.4 | 2.8 | 0.48 | | |
| 110 | 226 | 340 | 310 | 250 | 20 | 24 | 2.0 | 10.4 | 2.8 | 0.48 | 16 | |
| 115 | 221 | 339 | 311 | 249 | | | | | | | | |
| 120 | 220 | 338 | 309 | 248 | | | | | | | | |
| 121 | | | | | | | | | | | 17 | |
| Avg. | 248 | 337 | 302 | 240 | 20 | 24 | 2.0 | | | | | |

Table V
Original Data
Run E-1

| Time Mins. | A | B | C | D | E | F | G | N | M | J | L | K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 213 | 391 | 334 | 293 | 19 | 24 | | 35.0 | | 1.40 | | |
| 1.5 | 271 | 387 | 335 | 288 | | | | 17.0 | | 0.70 | | 1 |
| 5 | | | | | | | | | | | 1 | |
| 6 | 281 | 385 | 338 | 288 | | | | | | 0.61 | | |
| 10 | | | | | | | | | | | 2 | |
| 11 | 281 | 386 | 338 | 286 | | | 2.0 | 12.8 | 3.2 | 0.44 | | |
| 14 | 275 | 385 | 338 | 286 | | | | | | | | |
| 15 | | | | | | | | | | | 3 | |
| 17.5 | 271 | 385 | 339 | 286 | | | 2.0 | 11.6 | 3.0 | 0.44 | | |
| 20 | 269 | 387 | 340 | 287 | | | | | | | 4 | |
| 22.5 | 267 | 386 | 340 | 287 | | | 2.0 | 11.8 | 3.2 | 0.44 | | |
| 25 | 260 | 387 | 338 | 288 | | | | | | | 5 | |
| 27.5 | 258 | 384 | 338 | 286 | 19 | 24 | 2.0 | 12.2 | 2.8 | 0.40 | | |
| 30 | 252 | 385 | 338 | 286 | | | | | | | 6 | |
| 35 | 247 | 385 | 336 | 286 | | | 2.0 | 11.6 | 2.8 | 0.40 | | 2 |
| 40 | 241 | 384 | 338 | 286 | | | 2.0 | 11.6 | 2.8 | 0.40 | 7 | |
| 45 | 237 | 386 | 340 | 288 | | | | | | | | |
| 50 | 230 | 385 | 338 | 287 | | | 2.0 | 11.8 | 2.8 | 0.40 | 8 | 3 |
| 55 | 225 | 383 | 336 | 285 | | | | | | | | |
| 60 | 226 | 385 | 341 | 289 | | | 2.0 | 11.6 | 2.8 | 0.40 | 9 | |
| 65 | 224 | 386 | 339 | 287 | | | | | | | | |
| 70 | 221 | 383 | 340 | 288 | 20 | 24 | 2.0 | 11.6 | 2.8 | 0.40 | 10 | |
| 75 | 225 | 391 | 349 | 293 | | | 2.0 | 12.0 | 2.8 | 0.40 | | |
| 80 | 216 | 385 | 343 | 294 | | | 2.0 | 12.2 | 2.8 | 0.40 | | |
| 85 | 214 | 383 | 342 | 294 | | | | | | | 11 | |
| 90 | 215 | 387 | 348 | 296 | 20 | 24 | 2.0 | 12.4 | 2.8 | 0.40 | | |
| 95 | 211 | 385 | 348 | 296 | | | | | | | | |
| 99 | | | | | | | | | | | | |
| 100 | 206 | 383 | 347 | 298 | 20 | 24 | 2.0 | 11.8 | 2.8 | 0.35 | 12 | 4 |
| Avg. | 241 | 385 | 340 | 289 | 19.5 | 24 | 2.0 | 11.9 | | | | |

Table VI
Uncorrected Weight Balance
Run C-2
March 3, 1948

| | |
|---|---|
| Weight of Charge | 400 grams |
| Weight of Residue | 313 grams |
| Weight of Cyclone Separate | 3 grams |
| Weight of Distillate | 13.3 grams |
| Weight of Gas and Loss | 70.7 grams |

Residue was chocolate brown in color with a few uncarbonized particles remaining. Operation was smooth but ethylene dibromide was ejected from the static pressure manometer by the first surge of gas. Mercury was substituted at the end of the run. The capillary meter worked well but a brown viscous liquid was deposited on the entrance and exit lines.

Table VII
Uncorrected Weight Balance
Run A-4
January 29, 1948

| | |
|---|---|
| Weight of Charge | 500 grams |
| Weight of Charcoal Yield | 368 grams |
| Weight of Cyclone Separate | 8.5 grams |
| Weight of Distillate | 39 grams |
| Weight of Gas and Loss | 84.5 grams |

Residue was almost entirely carbonized with very, very few particles of uncarbonized sawdust remaining. Operation was smooth and satisfactory.

16.8 grams were recovered from the apparatus upon cleaning.

Table VIII
Uncorrected Weight Balance
Run B-2
February 11, 1948

| | |
|---|---|
| Weight of Charge | 400 grams |
| Weight of Charcoal residue | 229 grams |
| Weight of Cyclone Separate | 25 grams |
| Weight of Distillate | 50.3 grams |
| Weight of Gas and Loss | 95.7 grams |

Residue from reactor almost entirely carbonized to a dark black color. It was noticed that small spheres of carbonized sawdust from 3 mm to 6 mm in diameter were formed. However, a relatively small percentage of the total residue was in this form. Some trouble was noted in that the line leading from the reactor to the cyclone separator clogged once towards the end of the run. The top two plug valves and the slide valve were removed and the interior was inspected as well as possible. No tar was evident around the top of the reactor but grayish, slightly carbonized sawdust was adhering to the top section. The line leading from the reactor to the cyclone separator was almost completely clogged with a sticky, black tar which could not be scraped out. It was burned out but the line was not entirely cleared.

Table IX
Uncorrected Weight Balance
Run D-1
March 22, 1948

| | |
|---|---|
| Weight of Charge | 400 grams |
| Weight of Residue | 177 grams |
| Weight of Cyclone Separate | 13 grams |
| Weight of Distillate | 56 grams |
| Weight of Gas and Loss | 154 grams |

Residue was dark black in color and showed no uncarbonized particles.

Operation was smooth with nothing noted of particular interest. The cyclone separate was black and tar-like in character.

Table X
Uncorrected Weight Balance
Run E-1
April 1, 1948

| | |
|---|---|
| Weight of Charge | 400 grams |
| Weight of Residue | 120 grams |
| Weight of Cyclone Separate | 25.5 grams |
| Weight of Distillate | 56.0 grams |
| Weight of Gas and Loss | 198.5 grams |

The residue was charcoal dust entirely carbonized. The cyclone separate was tar-like and black in color.

Table XI
Liquid and Gas Analysis
Run C-2

| Time Mins. | Distillate yield grams | Cumulative yield grams | Acid yield m.e. | Cumulative yield m.e. | Wt.% as Acetic Acid | No methanol was found |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | | |
| 3 | 3.89 | 3.89 | 3.85 | 3.85 | 5.95 | |
| 8 | 1.38 | 5.28 | 2.03 | 5.88 | 8.83 | |
| 13 | 0.71 | 5.99 | 1.19 | 7.07 | 10.05 | |
| 18 | 0.52 | 6.51 | 0.75 | 7.82 | 8.68 | |
| 23 | 0.99 | 7.50 | 1.67 | 9.49 | 10.01 | |
| 28 | 0.50 | 8.00 | 1.01 | 10.50 | 12.12 | |
| 33 | 0.37 | 8.37 | 0.94 | 11.44 | 15.23 | |
| 43 | 0.57 | 8.94 | 1.58 | 13.02 | 16.65 | |
| 53 | 0.75 | 9.69 | 1.45 | 14.47 | 11.61 | |
| 63 | 0.52 | 10.21 | 1.35 | 15.82 | 15.58 | |
| 73 | 0.72 | 10.93 | 1.60 | 17.42 | 13.33 | |
| 83 | 0.51 | 11.44 | 1.37 | 18.79 | 16.13 | |
| 93 | 0.29 | 11.73 | 1.11 | 19.90 | 23.00 | |
| 103 | 0.69 | 12.42 | 1.12 | 21.02 | 9.75 | |
| 113 | 0.35 | 12.77 | 1.03 | 22.05 | 17.68 | |
| 123 | 0.20 | 12.97 | 0.89 | 22.94 | 26.65 | |
| 133 | 0.18 | 13.15 | 0.61 | 23.55 | 20.30 | |
| 143 | 0.19 | 13.34 | 0.47 | 24.02 | 14.83 | |

Avg. 13.32

| Time Mins. | % CO | % $CO_2$ | % $N_2$ | M.W. of gas |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 5 | 1.25 | 0.50 | 98.25 | 28.02 |
| 9 | Analysis unusable | | | |
| 15 | 0 | 4.00 | 96.00 | 28.65 |
| 25 | 0 | 0 | 100.0 | 28.00 |
| 29 | 1.49 | 0.21 | 98.30 | 28.01 |
| 35 | 0 | 0.20 | 99.80 | 28.01 |

Average M.W. 28.2

Table XII
Liquid and Gas Analysis
Run A-4

| Time Mins. | Distillate yield grams | Cumulative yield grams | Acid yield m.e. | Cumulative acid yield | Wt. % as Acetic Acid |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | |
| 16 | 8.20 | 8.20 | 11.59 | 11.59 | 8.49 |
| 23 | 4.00 | 12.20 | 8.78 | 20.37 | 13.15 |
| 30 | 5.00 | 17.20 | 14.11 | 34.48 | 16.92 |
| 40 | 3.85 | 21.05 | 11.06 | 45.54 | 17.22 |
| 53 | 4.96 | 26.01 | 13.94 | 59.48 | 16.85 |
| 68 | 3.00 | 29.01 | 10.33 | 69.81 | 20.67 |
| 83 | 2.78 | 31.79 | 10.19 | 80.00 | 22.00 |
| 98 | 1.80 | 33.50 | 6.99 | 86.99 | 23.30 |
| 113 | 1.90 | 35.40 | 6.65 | 93.64 | 21.00 |
| 128 | 1.80 | 37.20 | 8.54 | 102.18 | 28.20 |
| 143 | 0.80 | 38.00 | 3.15 | 105.33 | 23.70 |
| 158 | 0.45 | 38.45 | 1.22 | 106.55 | 16.28 |
| 173 | 0.20 | 38.65 | 2.45 | 109.00 | 7.70 |

Avg. 18.11

| Time | | | |
|---|---|---|---|
| 5 | CO - 0.0% | $CO_2$ - 0.0% | $N_2$ - 100% |
| | | Average M.W. = 28.0 | |
| 15 | CO - 0.0% | $CO_2$ - 0.0% | $N_2$ - 100.0% |
| | | Average M.W. = 28.0 | |
| 24 | CO - 0.0% | $CO_2$ - 0.0% | $N_2$ - 100.0% |
| | | Average M.W. = 28.0 | |
| 53 | CO - 0.0% | $CO_2$ - 0.0% | $N_2$ - 100.0% |
| | | Average M.W. = 28.0 | |
| 83 | CO - 0.0% | $CO_2$ - 3.4% | $N_2$ - 96.6% |
| | | Average M.W. = 28.5 | |
| 188 | CO - 0.8% | $CO_2$ - 0.0% | $N_2$ - 99.2% |
| | | Average M.W. = 28.0 | |

Average Molecular Weight
of Gas over run - 28.1

Table XIII
Liquid and Gas Analysis
Run B-2

| Time Mins. | Distillate yield grams | Cumulative yield grams | Acid yield m.e. | Cumulative acid yield m.e. | Methanol grams | Accum. Methanol grams | Mol % | Weight % as Acetic Acid |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | | |
| 6 | 10.32 | 10.32 | 27.45 | 27.45 | | | | 15.97 |
| 10 | 9.70 | 20.02 | 29.48 | 56.93 | .194 | .194 | .54 | 18.25 |
| 15 | 5.72 | 25.74 | 17.47 | 74.40 | | | | 18.32 |
| 20 | 3.86 | 29.60 | 13.15 | 87.55 | | | | 20.45 |
| 25 | 4.20 | 33.80 | 14.37 | 101.92 | .172 | .366 | .71 | 20.50 |
| 30 | 2.96 | 36.76 | 10.52 | 112.44 | | | | 19.26 |
| 35 | 3.05 | 39.81 | 12.69 | 125.13 | | | | 24.95 |
| 44 | 1.88 | 41.69 | 7.55 | 132.68 | | | | 24.10 |
| 54 | 1.14 | 42.83 | 4.48 | 137.16 | .229 | .595 | 1.44 | 23.60 |
| 64 | 1.11 | 43.94 | 4.63 | 141.79 | | | | 25.00 |
| 74 | 0.37 | 44.31 | 2.56 | 144.35 | | | | 41.60 |
| 84 | 0.64 | 44.95 | 2.70 | 147.50 | | | | 25.30 |
| 94 | 0.48 | 45.43 | 2.28 | 149.33 | | | | 28.50 |
| 104 | 0.29 | 45.72 | 1.29 | 150.61 | | | | 26.50 |
| 114 | 0.27 | 45.99 | 1.37 | 151.98 | | | | 30.50 |
| | | | | | | | Avg. | 19.80 |

Gas analysis showed no gas except nitrogen.

Table XIV
Liquid and Gas Analysis
Run D-1

| Time Mins. | Distillate yield grams | Cumulative yield grams | Acid yield m.e. | Cumulative Acid yield m.e. | Methanol grams | Cumulative yield grams | Mol % Methanol | Wt. % as Acetic Acid |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | | |
| 7 | 23.45 | 23.45 | 55.50 | 55.50 | 0.485 | 0.485 | 2.07 | 14.20 |
| 10 | 8.30 | 31.75 | 25.10 | 80.60 | | | | 18.18 |
| 15 | 6.36 | 38.11 | 20.10 | 100.70 | | | | 18.92 |
| 20 | 3.84 | 41.95 | 12.00 | 112.70 | 0.694 | 1.179 | 3.75 | 18.77 |
| 25 | 3.35 | 45.30 | 10.60 | 123.30 | | | | 18.98 |
| 30 | 2.73 | 48.03 | 9.00 | 132.30 | | | | 19.78 |
| 35 | 1.61 | 49.64 | 5.01 | 137.31 | | | | 18.70 |
| 40 | 1.26 | 50.90 | 4.11 | 141.42 | | | | 19.55 |
| 45 | 1.04 | 51.94 | 3.27 | 144.69 | | | | 15.88 |
| 50 | 0.77 | 52.71 | 2.48 | 147.17 | | | | 31.30 |
| 60 | 1.08 | 53.79 | 3.54 | 150.71 | 0.639 | 1.818 | 4.98 | 20.20 |
| 70 | 0.64 | 54.43 | 2.67 | 153.38 | | | | 25.00 |
| 80 | 0.54 | 54.97 | 1.87 | 155.25 | | | | 20.80 |
| 90 | 0.41 | 55.38 | 1.46 | 156.71 | | | | 21.40 |
| 100 | 0.27 | 55.65 | 1.00 | 157.71 | | | | 22.20 |
| 110 | 0.29 | 55.94 | 1.11 | 158.82 | | | | 22.93 |
| 120 | 0.17 | 56.11 | 0.67 | 159.49 | | | | 23.65 |
| | | | | | | | Avg. | 20.61 |

| Time | % CO | % $CO_2$ | % $N_2$ | Avg. M.W. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 7 | 29.5 | 44.2 | 26.3 | 35.05 |
| 30 | 51.1 | 23.5 | 25.4 | 31.75 |
| 65 | 0 | 0.1 | 99.9 | 28.00 |

Table XV
Liquid and Gas Analysis
Run E-1

| Time Mins. | Distillate yield grams | Cumulative yield grams | Acid yield m.e. | Cumulative yield m.e. | Methanol yield | Mol % Methanol | Wt. % as Acetic Acid |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | | | |
| 5 | 32.18 | 32.18 | 87.75 | 87.75 | 2.381 | 7.4 | 16.40 |
| 10 | 7.92 | 40.11 | 23.50 | 111.25 | | | 17.82 |
| 15 | 6.74 | 46.85 | 21.84 | 133.09 | | | 19.47 |
| 20 | 2.65 | 49.50 | 8.32 | 141.41 | | | 18.86 |
| 25 | 2.06 | 51.56 | 6.36 | 147.77 | | | 18.53 |
| 30 | 0.91 | 52.47 | 3.04 | 150.81 | | | 20.03 |
| 40 | 1.10 | 53.57 | 3.12 | 153.93 | | | 17.00 |
| 50 | 0.54 | 54.11 | 2.15 | 156.08 | | | 23.90 |
| 60 | 0.67 | 54.78 | 2.19 | 158.27 | | | 19.63 |
| 70 | 0.39 | 55.17 | 1.32 | 159.59 | | | 20.30 |
| 85 | 0.59 | 55.76 | 1.86 | 161.45 | | | 19.25 |
| 100 | 0.22 | 55.98 | 0.79 | 162.24 | | | 21.55 |
| | | | | | | Avg. | 19.39 |

| Time | % CO | $\%CO_2$ | $\% N_2$ | Avg. M.W. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1.5 | 52.6 | 28.4 | 20.0 | 32.80 |
| 30 | 2.8 | 7.1 | 90.1 | 29.12 |
| 47 | 0 | 0 | 100.0 | 28.0 |
| 99 | 0.6 | 1.9 | 97.5 | 28.30 |

Table XVI
Rate of Vaporization of Products
Run C-2

| Time in Mins. | Gms. per min. of water | Gms. per min. of acid | Gm. mols of gas per min. |
|---|---|---|---|
| 0 | 0 | | |
| 3 | .2040 | .0810 | .0323 |
| 4 | .2040 | .0810 | .0323 |
| 8 | .2040 | .0810 | .0323 |
| 10 | .1957 | .0785 | .0012 |
| 13 | .2040 | .0810 | .0323 |
| 18 | .1892 | .0743 | .0000 |
| 23 | .2040 | .0810 | .0323 |
| 28 | .1892 | .0743 | .0000 |
| 33 | .2040 | .0810 | .0323 |
| 38 | .2040 | .0810 | .0323 |
| 48 | .1957 | .0785 | .0012 |
| 53 | .2040 | .0810 | .0323 |
| 63 | .1957 | .0785 | .0012 |
| 73 | .1957 | .0785 | .0012 |
| 83 | .2040 | .0810 | .0323 |
| 98 | .1957 | .0785 | .0012 |
| 103 | .1892 | .0743 | .0000 |
| 108 | .1892 | .0743 | .0000 |
| 113 | .1892 | .0743 | .0000 |
| 118 | .1957 | .0785 | .0012 |
| 123 | .1892 | .0743 | .0000 |
| 143 | .1892 | .0743 | .0000 |
| Avg. | .1989 | .0784 | .0136 |

Inlet Flow - $31.5\sqrt{2}$ - 44.6 Gm. mols

Exit Flow - $15\sqrt{\Delta P}$

Inlet Temperature - 21° C.

Exit Temperature - 17° C.

Partial pressure of Acetic Acid - 1.3 mm

Partial pressure of water - 12.6 mm

Table XVII
Rate of Vaporization of Products
Run A-4

| Time in Mins. | Gms. per min. of water | Gms. per min. of acid | Gm. mols of gas per min. |
|---|---|---|---|
| 0 | 0 | 0 | |
| 3 | .1412 | .0756 | .017 |
| 8 | .1412 | .0756 | .017 |
| 13 | .1412 | .0756 | .017 |
| 25 | .1412 | .0756 | .017 |
| 30 | .1370 | .0733 | .000 |
| 38 | .1412 | .0756 | .017 |
| 43 | .1412 | .0756 | .017 |
| 58 | .1412 | .0756 | .017 |
| 63 | .1412 | .0756 | .017 |
| 68 | .1412 | .0756 | .017 |
| 73 | .1370 | .0733 | .000 |
| 83 | .1412 | .0756 | .017 |
| 88 | .1460 | .0781 | .025 |
| 98 | .1460 | .0781 | .025 |
| 108 | .1460 | .0781 | .025 |
| 118 | .1460 | .0781 | .025 |
| 138 | .1460 | .0781 | .025 |
| 143 | .1460 | .0781 | .025 |
| 153 | .1460 | .0781 | .025 |
| 158 | .1460 | .0781 | .025 |
| 168 | .1530 | .0825 | .025 |
| 173 | .1530 | .0825 | .025 |
| 188 | .1530 | .0825 | .025 |
| Avg. | .1441 | .0771 | .0208 |

Inlet flow - 44.5 gm. mols/hr.

Exit flow - $35.7\sqrt{\Delta P}$

Inlet Temperature - 21.5° C.

Condenser Temprature - 11° C.

Partial pressure of Acetic Acid and water from Chart XXV is 9.4 mm

Partial pressure of $H_2O$ is 8.1 mm

Partial pressure of Acetic Acid is 1.3 mm

Table XVIII
Rate of Vaporization of Products
Run B-2

| Time in Mins. | Gms. per min. of Water Vapor | Gms. per min. of Acid Vapor | Gms. per min. of Methanol | Gm. mols per min. of Gas |
|---|---|---|---|---|
| 0 | 0 | | | |
| 1 | .1552 | .0975 | .0358 | .0133 |
| 4 | .1552 | .0975 | .0358 | .0133 |
| 9 | .1552 | .0975 | .0358 | .0133 |
| 14 | .1552 | .0975 | .0358 | .0133 |
| 18 | .1640 | .1050 | .0358 | .0227 |
| 22 | .1640 | .1050 | .0358 | .0227 |
| 28 | .1552 | .0975 | .0440 | .0133 |
| 37 | .1507 | .0945 | .0409 | .0050 |
| 40 | .1640 | .1050 | .0398 | .0227 |
| 53 | .1460 | .0917 | .0384 | .0000 |
| 58 | .1552 | .0975 | .0455 | .0133 |
| 59 | .1640 | .1050 | .0480 | .0227 |
| 61 | .1640 | .1050 | .0480 | .0227 |
| 99 | .1552 | .0975 | .0455 | .0133 |
| 114 | .1460 | .0917 | .0427 | .0000 |
| Avg. | .1566 | .0990 | .0405 | .0141 |

Inlet flow - 44.4 gm. mols/hr.

Exit flow - $35.5\sqrt{\Delta P}$

Condenser Temperature - 12° C.

Inlet Temperature - 20° C.

Partial pressure of Acetic Acid and Water from Chart XXV - 10.1 mm

Partial pressure of Methanol - 2.5 mm

Partial pressure of Water - 8.5 mm

Partial pressure of Acid - 1.6 mm

Table XIX
Rate of Vaporization of Products
Run D-1

| Time in Mins. | Gms. per min. of Water | Gms. per min. of Acid | Gms. per min. of Methanol | Gm. mols per min. of Gas |
|---|---|---|---|---|
| 0 | | | | |
| 3 | 0.3680 | .3180 | .121 | .414 |
| 20 | 0.279 | .2420 | .137 | .117 |
| 25 | 0.256 | .2230 | .126 | .055 |
| 30 | 0.256 | .2230 | .126 | .050 |
| 35 | 0.259 | .2240 | .127 | .085 |
| 40 | 0.259 | .2240 | .127 | .085 |
| 45 | 0.250 | .2175 | .123 | .022 |
| 50 | 0.253 | .2200 | .124 | .042 |
| 60 | 0.258 | .2250 | .172 | .051 |
| 65 | 0.263 | .2285 | .174 | .062 |
| 70 | 0.261 | .2270 | .173 | .060 |
| 75 | 0.253 | .2205 | .168 | .055 |
| 80 | 0.261 | .2270 | .173 | .060 |
| 90 | 0.263 | .2285 | .174 | .066 |
| 100 | 0.256 | .2230 | .170 | .047 |
| 105 | 0.256 | .2230 | .170 | .047 |
| 110 | 0.256 | .2230 | .170 | .047 |
| Avg. | .2289 | .2249 | .150 | .0556 |

Inlet flow - 44.3

Exit flow - $15.0\sqrt{\frac{28}{MW}\Delta P}$

Inlet Temperature - 24° C.

Condenser Temperature - 20° C.

Partial pressure of Water - 13.8 mm

Partial pressure of Acid - 3.1 mm

Table XX
Rate of Vaporization of Products
Run E-1

| Time in Mins. | Gms. per min. of Water | Gms. per min. of Acid | Gms. per min of Methanol | Gm. mols per min. of Gas |
|---|---|---|---|---|
| 0 | .437 | .313 | .420 | .614 |
| 1.5 | .306 | .219 | .294 | .181 |
| 11 | .268 | .192 | .258 | .072 |
| 17.5 | .260 | .186 | .249 | .046 |
| 22.5 | .263 | .188 | .254 | .058 |
| 27.5 | .270 | .193 | .259 | .067 |
| 35 | .268 | .192 | .257 | .068 |
| 40 | .270 | .193 | .259 | .067 |
| 50 | .275 | .197 | .264 | .083 |
| 60 | .273 | .195 | .262 | .081 |
| 70 | .273 | .195 | .262 | .081 |
| 75 | .277 | .198 | .266 | .100 |
| 80 | .279 | .200 | .268 | .106 |
| 90 | .282 | .201 | .271 | .112 |
| 100 | .275 | .197 | .264 | .080 |
| Avg. | .2742 | .2039 | .2632 | .0859 |

Inlet Temperature - 24° C.

Condenser Temperature - 19.5° C.

Inlet flow - 44.3

Exit flow - $15.3\sqrt{\frac{28}{MW}(\Delta P)}$

Partial pressure of Water - 13.5 mm

Partial pressure of Acetic Acid - 2.9 mm

Partial pressure of Methanol - 7.3 mm

Table XXI
Corrected Yields
Run C-2

| Time in Mins. | Corrected Distillate yield in grams | Corrected Acid yield in m.e. | Distillate yield based on 1000 grams of charge | Acid yield based on 1000 grams of charge |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | |
| 3 | 4.71 | 7.75 | 11.79 | 19.37 |
| 8 | 7.46 | 16.28 | 18.65 | 40.70 |
| 13 | 9.44 | 23.97 | 23.60 | 59.92 |
| 18 | 11.42 | 31.32 | 28.55 | 78.30 |
| 23 | 13.78 | 39.39 | 34.45 | 98.47 |
| 28 | 15.64 | 46.90 | 39.10 | 117.25 |
| 33 | 17.37 | 54.34 | 43.42 | 135.85 |
| 43 | 20.66 | 68.92 | 51.65 | 172.30 |
| 53 | 24.16 | 83.37 | 60.40 | 208.42 |
| 63 | 27.41 | 97.72 | 68.53 | 244.30 |
| 73 | 30.83 | 112.42 | 77.07 | 281.05 |
| 83 | 34.07 | 126.79 | 85.17 | 316.97 |
| 93 | 37.13 | 140.90 | 92.82 | 352.25 |
| 103 | 40.52 | 155.02 | 101.30 | 387.55 |
| 113 | 43.57 | 168.85 | 108.92 | 422.12 |
| 123 | 46.57 | 182.94 | 116.42 | 457.30 |
| 133 | 49.48 | 196.55 | 123.70 | 491.37 |
| 143 | 52.34 | 209.82 | 130.85 | 524.55 |

Table XXII
Corrected Yields
Run A-4

| Time in Mins. | Corrected Distillate yield in grams | Corrected Acid yield in m.e. | Distillate yield based on 1000 grams of charge | Acid yield based on 1000 grams of charge |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 16 | 11.74 | 32.17 | 23.48 | 64.34 |
| 23 | 17.29 | 48.95 | 34.58 | 97.90 |
| 30 | 23.83 | 73.03 | 47.66 | 146.06 |
| 40 | 29.90 | 96.94 | 59.80 | 193.88 |
| 53 | 37.73 | 127.58 | 75.46 | 255.16 |
| 68 | 44.04 | 157.21 | 88.08 | 314.42 |
| 83 | 50.14 | 186.50 | 100.28 | 373.00 |
| 98 | 55.18 | 212.99 | 110.36 | 425.98 |
| 113 | 60.40 | 238.84 | 120.80 | 477.68 |
| 128 | 56.50 | 266.58 | 131.00 | 533.16 |
| 143 | 69.60 | 288.83 | 139.20 | 577.66 |
| 158 | 73.37 | 309.55 | 146.74 | 619.10 |
| 173 | 76.87 | 331.20 | 153.76 | 662.40 |

Table XXIII
Corrected Yields
Run B-2

| Time in Mins. | Corrected Distillate yield in grams | Corrected Acid yield in m.e. | Distillate yield based on 1000 grams of charge | Acid yield based on 1000 grams of charge | Corrected Methanol yield in grams | Methanol yield based on 1000 grams |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 12.10 | 37.35 | 30.24 | 93.40 | | |
| 10 | 22.98 | 73.43 | 62.50 | 183.30 | 0.599 | 1.50 |
| 15 | 30.19 | 99.17 | 75.40 | 248.00 | | |
| 20 | 35.53 | 120.55 | 88.90 | 301.20 | | |
| 25 | 41.21 | 143.17 | 103.00 | 356.00 | 1.376 | 3.44 |
| 30 | 45.65 | 161.94 | 114.00 | 405.00 | | |
| 35 | 50.19 | 182.83 | 125.60 | 457.00 | | |
| 44 | 54.73 | 205.28 | 137.00 | 513.00 | | |
| 54 | 58.83 | 226.26 | 147.00 | 566.00 | 2.785 | 6.96 |
| 64 | 62.90 | 247.39 | 157.10 | 619.00 | | |
| 74 | 66.21 | 266.35 | 165.60 | 666.00 | | |
| 84 | 69.85 | 285.45 | 174.40 | 713.00 | | |
| 94 | 73.26 | 304.33 | 183.00 | 761.00 | | |
| 104 | 76.52 | 322.31 | 191.60 | 806.00 | | |
| 114 | 79.79 | 340.18 | 199.40 | 855.00 | 5.205 | 13.00 |

Table XXIV
Corrected Yields
Run D-1

| Time in Mins. | Corrected Distillate yield in grams | Corrected Acid yield in m.e. | Distillate yield based on 1000 grams of charge | Acid yield based on 1000 grams of charge | Corrected Methanol yield in grams | Methanol yield based on 1000 grams |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | | |
| 7 | 27.88 | 81.70 | 69.80 | 204.80 | 1.54 | 3.85 |
| 10 | 38.08 | 118.10 | 95.10 | 295.00 | | |
| 15 | 47.61 | 156.90 | 119.00 | 392.00 | | |
| 20 | 54.61 | 187.70 | 136.60 | 469.00 | 4.18 | 10.45 |
| 25 | 61.11 | 217.05 | 152.80 | 542.00 | | |
| 30 | 67.01 | 244.70 | 167.60 | 611.00 | | |
| 35 | 71.79 | 268.61 | 179.40 | 646.00 | | |
| 40 | 76.20 | 291.42 | 190.70 | 729.00 | | |
| 45 | 80.44 | 313.39 | 201.00 | 783.00 | | |
| 50 | 84.31 | 334.87 | 210.90 | 837.50 | | |
| 60 | 91.75 | 375.71 | 228.40 | 943.00 | 10.82 | 27.05 |
| 70 | 98.73 | 415.38 | 246.80 | 1040.00 | | |
| 80 | 105.57 | 455.25 | 264.00 | 1137.00 | | |
| 90 | 112.38 | 494.71 | 280.80 | 1237.00 | | |
| 100 | 118.95 | 532.71 | 297.40 | 1331.00 | | |
| 110 | 125.54 | 571.82 | 314.00 | 1430.00 | | |
| 120 | 132.11 | 609.49 | 330.50 | 1524.00 | 19.82 | 49.60 |

Table XXV
Corrected Yields
Run E-1

| Time in Mins. | Corrected Distillate yield in grams | Corrected Acid yield in m.e. | Distillate yield based on 1000 grams of charge | Acid yield based on 1000 grams of charge | Corrected Methanol yield in grams | Methanol yield based on 1000 grams |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 35.89 | 104.75 | 89.80 | 262.00 | 3.69 | 9.23 |
| 10 | 47.52 | 145.25 | 118.90 | 363.00 | | |
| 15 | 57.96 | 184.09 | 145.00 | 460.00 | | |
| 20 | 63.83 | 209.41 | 159.60 | 524.00 | | |
| 25 | 70.08 | 232.77 | 175.20 | 581.50 | | |
| 30 | 74.69 | 252.81 | 186.70 | 631.00 | | |
| 40 | 83.22 | 289.93 | 208.00 | 725.00 | | |
| 50 | 91.22 | 326.08 | 228.00 | 815.00 | | |
| 60 | 99.28 | 362.27 | 248.00 | 906.00 | | |
| 70 | 107.07 | 407.59 | 268.00 | 1020.00 | | |
| 85 | 118.76 | 450.45 | 296.60 | 1135.00 | | |
| 100 | 130.11 | 502.24 | 325.20 | 1256.00 | 30.46 | 76.18 |

Table XXVI
Distillate Correlations
Run C-2

| Time in Mins. $\theta$ | Distillate yield in grams L | Change in yield of distillate $\Delta L$ | Rate of change of yield $\Delta L/\Delta\theta$ | Average yield of distillate L avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | | |
| 3 | 11.79 | 11.70 | 3.93 | 5.89 |
| 8 | 18.65 | 6.86 | 1.37 | 15.22 |
| 13 | 23.60 | 4.95 | 0.99 | 21.12 |
| 18 | 28.55 | 4.95 | 0.99 | 26.07 |
| 23 | 34.45 | 5.90 | 1.18 | 31.50 |
| 28 | 39.10 | 4.65 | 0.93 | 36.77 |
| 33 | 43.42 | 4.32 | 0.86 | 41.26 |
| 43 | 51.65 | 8.23 | 0.82 | 47.54 |
| 53 | 60.40 | 8.75 | 0.87 | 56.02 |
| 63 | 68.53 | 8.13 | 0.81 | 64.46 |
| 73 | 77.07 | 8.54 | 0.85 | 72.80 |
| 83 | 85.17 | 8.10 | 0.81 | 81.12 |
| 93 | 92.82 | 7.65 | 0.76 | 88.99 |
| 103 | 101.30 | 8.48 | 0.85 | 97.06 |
| 113 | 108.92 | 7.62 | 0.76 | 105.11 |
| 123 | 116.42 | 7.50 | 0.75 | 112.67 |
| 133 | 123.70 | 7.28 | 0.73 | 120.06 |
| 143 | 130.85 | 7.15 | 0.71 | 127.27 |

Table XXVII
Acid Correlations
Run C-2

| Time in Mins. $\theta$ | Acid yield in m.e. A | Change in yield of acid $\Delta A$ | Rate of change of yield $\Delta A/\Delta\theta$ | Average yield of Acid A avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | |
| 3 | 19.37 | 19.37 | 6.46 | 9.68 |
| 8 | 40.70 | 21.33 | 4.26 | 30.03 |
| 13 | 59.92 | 19.22 | 3.84 | 50.31 |
| 18 | 78.30 | 18.38 | 3.68 | 69.11 |
| 23 | 98.47 | 20.17 | 4.03 | 88.38 |
| 28 | 117.25 | 18.78 | 3.75 | 107.86 |
| 33 | 135.85 | 18.60 | 3.72 | 126.55 |
| 43 | 172.30 | 36.45 | 3.64 | 154.07 |
| 53 | 208.42 | 36.12 | 3.61 | 190.36 |
| 63 | 244.30 | 35.88 | 3.59 | 226.36 |
| 73 | 281.05 | 36.75 | 3.67 | 262.67 |
| 83 | 316.97 | 36.92 | 3.69 | 299.51 |
| 93 | 352.25 | 35.28 | 3.53 | 334.61 |
| 103 | 387.55 | 35.30 | 3.53 | 369.90 |
| 113 | 422.12 | 34.57 | 3.46 | 404.83 |
| 123 | 457.30 | 35.18 | 3.52 | 439.71 |
| 133 | 491.37 | 34.07 | 3.41 | 474.33 |
| 143 | 524.55 | 33.18 | 3.32 | 507.91 |

Table XXVIII
Distillate Correlations
Run A-4

| Time in Mins. $\theta$ | Distillate yield in grams L | Change in yield grams $\Delta L$ | Rate of change of yield $\Delta L/\Delta\theta$ | Average yield L avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 16 | 23.48 | 23.48 | 1.466 | 11.72 |
| 23 | 34.58 | 11.10 | 1.585 | 29.03 |
| 30 | 47.66 | 13.08 | 1.870 | 41.12 |
| 40 | 59.80 | 12.14 | 1.214 | 53.73 |
| 53 | 75.46 | 15.66 | 1.204 | 67.63 |
| 68 | 88.08 | 12.62 | .841 | 81.77 |
| 83 | 100.28 | 12.20 | .814 | 94.18 |
| 98 | 110.36 | 10.08 | .672 | 105.32 |
| 113 | 120.80 | 10.44 | .696 | 115.58 |
| 128 | 131.00 | 10.20 | .680 | 125.90 |
| 143 | 139.20 | 8.20 | .546 | 135.10 |
| 158 | 146.74 | 7.54 | .502 | 142.97 |
| 173 | 153.76 | 7.02 | .469 | 150.21 |

Table XXIX
Acid Correlations
Run A-4

| Time in Mins. $\theta$ | Acid yield in m.e. A | Change in yield in m.e. $\Delta A$ | Rate of change of yield $\Delta A/\Delta\theta$ | Average yield A avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 16 | 64.34 | 64.34 | 4.02 | 32.17 |
| 23 | 97.90 | 33.56 | 4.79 | 81.12 |
| 30 | 146.06 | 48.16 | 6.88 | 121.98 |
| 40 | 193.88 | 47.82 | 4.78 | 169.97 |
| 53 | 255.16 | 61.28 | 4.71 | 224.52 |
| 68 | 314.42 | 59.26 | 3.95 | 284.79 |
| 83 | 373.00 | 58.58 | 3.91 | 343.71 |
| 98 | 425.98 | 52.98 | 3.53 | 399.49 |
| 113 | 477.68 | 51.70 | 3.45 | 441.83 |
| 128 | 533.16 | 55.48 | 3.70 | 505.42 |
| 143 | 577.66 | 44.50 | 2.97 | 555.41 |
| 158 | 619.10 | 41.44 | 2.76 | 598.38 |
| 173 | 662.40 | 43.30 | 2.89 | 640.75 |

Table XXX
Distillate Correlations
Run B-2

| Time in Mins. $\theta$ | Distillate yield in grams L | Change in distillate yield $\Delta L$ | Rate of change of yield $\Delta L/\Delta\theta$ | Average yield L avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 6 | 30.24 | 30.24 | 5.04 | 15.12 |
| 10 | 62.50 | 32.26 | 8.06 | 46.37 |
| 15 | 75.40 | 12.90 | 2.58 | 68.95 |
| 20 | 88.90 | 13.50 | 2.70 | 82.15 |
| 25 | 103.00 | 14.10 | 2.82 | 95.95 |
| 30 | 114.00 | 11.00 | 2.20 | 108.50 |
| 35 | 125.60 | 11.60 | 2.32 | 119.80 |
| 44 | 137.00 | 11.40 | 1.26 | 131.30 |
| 54 | 147.00 | 10.00 | 1.00 | 142.00 |
| 64 | 157.10 | 10.10 | 1.01 | 152.05 |
| 74 | 165.60 | 8.50 | 0.85 | 161.35 |
| 84 | 174.40 | 8.80 | 0.88 | 170.00 |
| 94 | 183.00 | 8.60 | 0.86 | 178.70 |
| 104 | 191.60 | 8.60 | 0.86 | 187.30 |
| 114 | 199.40 | 7.80 | 0.78 | 195.50 |

Table XXXI
Acid Correlations
Run B-2

| Time in Mins. $\theta$ | Acid yield in m.e. A | Change in Acid yield $\Delta A$ | Rate of change of yield $\Delta A/\Delta\theta$ | Average yield A avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 6 | 93.40 | 93.40 | 15.56 | 46.70 |
| 10 | 183.30 | 89.90 | 22.25 | 138.35 |
| 15 | 248.00 | 64.70 | 12.94 | 215.65 |
| 20 | 301.20 | 53.20 | 10.64 | 274.60 |
| 25 | 356.00 | 54.80 | 10.96 | 328.60 |
| 30 | 405.00 | 49.00 | 9.80 | 380.50 |
| 35 | 457.00 | 50.00 | 10.00 | 430.00 |
| 44 | 513.00 | 56.00 | 6.22 | 485.00 |
| 54 | 566.00 | 53.00 | 5.30 | 539.50 |
| 64 | 619.00 | 53.00 | 5.30 | 592.50 |
| 74 | 666.00 | 47.00 | 4.70 | 642.50 |
| 84 | 713.00 | 47.00 | 4.70 | 689.50 |
| 94 | 761.00 | 48.00 | 4.80 | 737.00 |
| 104 | 806.00 | 45.00 | 4.50 | 783.50 |
| 114 | 855.00 | 49.00 | 4.90 | 830.50 |

Table XXXII
Methanol Correlations
Run B-2

| Time in Mins. $\theta$ | Methanol yield M | Change in yield $\Delta M$ | Rate of change of yield $\Delta M/\Delta\theta$ | Average yield M avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 10 | 1.50 | 1.50 | .150 | .75 |
| 25 | 3.44 | 1.94 | .130 | 2.47 |
| 54 | 6.96 | 3.52 | .120 | 5.20 |
| 114 | 13.00 | 6.04 | .120 | 9.98 |

Table XXXIII
Distillate Correlations
Run D-1

| Time in Mins. $\theta$ | Distillate yield in grams L | Change of yield $\Delta L$ | Rate of change of yield $\Delta L/\Delta\theta$ | Average yield L avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 7 | 69.80 | 69.80 | 9.97 | 34.90 |
| 10 | 95.10 | 25.30 | 8.43 | 82.45 |
| 15 | 119.00 | 23.90 | 4.78 | 107.05 |
| 20 | 136.60 | 17.60 | 3.52 | 127.80 |
| 25 | 152.80 | 16.20 | 3.24 | 144.70 |
| 30 | 167.60 | 14.80 | 2.96 | 160.20 |
| 35 | 179.40 | 11.80 | 2.36 | 173.50 |
| 40 | 190.70 | 11.30 | 2.26 | 185.05 |
| 45 | 201.00 | 10.30 | 2.06 | 195.85 |
| 50 | 210.90 | 9.90 | 1.98 | 205.95 |
| 60 | 228.40 | 17.50 | 1.75 | 219.65 |
| 70 | 246.80 | 18.40 | 1.84 | 237.60 |
| 80 | 264.00 | 17.20 | 1.72 | 255.40 |
| 90 | 280.80 | 16.80 | 1.68 | 272.40 |
| 100 | 297.40 | 16.60 | 1.66 | 289.10 |
| 110 | 314.00 | 16.60 | 1.66 | 305.70 |
| 120 | 330.50 | 16.50 | 1.65 | 322.25 |

Table XXIV
Acid Correlations
Run D-1

| Time in Mins. $\theta$ | Acid yield in m.e. A | Change in yield $\Delta A$ | Rate of change in yield $\Delta A/\Delta\theta$ | Average yield A avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 7 | 204.80 | 204.80 | 29.25 | 102.40 |
| 10 | 295.00 | 91.20 | 30.40 | 250.40 |
| 15 | 392.00 | 97.00 | 19.40 | 343.50 |
| 20 | 469.00 | 77.00 | 15.40 | 430.50 |
| 25 | 542.00 | 73.00 | 14.60 | 505.50 |
| 30 | 611.00 | 69.00 | 13.80 | 576.50 |
| 35 | 646.00 | 35.00 | 7.00 | 628.50 |
| 40 | 729.00 | 83.00 | 16.60 | 687.50 |
| 45 | 783.00 | 54.00 | 10.80 | 756.00 |
| 50 | 837.50 | 54.50 | 10.90 | 810.25 |
| 60 | 943.00 | 105.50 | 10.55 | 895.25 |
| 70 | 1040.00 | 97.00 | 9.70 | 991.50 |
| 80 | 1137.00 | 97.00 | 9.70 | 1098.50 |
| 90 | 1237.00 | 100.00 | 10.00 | 1187.00 |
| 100 | 1331.00 | 94.00 | 9.40 | 1284.00 |
| 110 | 1430.00 | 99.00 | 9.90 | 1380.50 |
| 120 | 1524.00 | 94.00 | 9.40 | 1477.00 |

Table XXXV
Methanol Correlations
Run D-1

| Time in Mins. $\theta$ | Methanol yield M | Change in yield $\Delta M$ | Rate of change in yield $\Delta M/\Delta\theta$ | Average yield M avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 7 | 3.85 | 3.85 | 0.55 | 1.92 |
| 20 | 10.45 | 6.60 | 0.51 | 7.15 |
| 60 | 27.05 | 16.60 | 0.415 | 18.75 |
| 120 | 49.06 | 22.01 | 0.367 | 38.05 |

Table XXXVI
Distillate Correlations
Run E-1

| Time in Mins. $\theta$ | Distillate yield in grams L | Change in yield $\Delta L$ | Rate of change of yield $\Delta L/\Delta\theta$ | Average yield L avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 5 | 89.80 | 89.80 | 17.96 | 44.90 |
| 10 | 118.90 | 29.10 | 5.82 | 104.35 |
| 15 | 145.00 | 26.10 | 5.22 | 131.95 |
| 20 | 159.60 | 14.60 | 2.92 | 152.30 |
| 25 | 175.20 | 23.60 | 4.72 | 171.40 |
| 30 | 186.70 | 11.50 | 2.30 | 180.95 |
| 40 | 208.00 | 21.30 | 2.13 | 197.35 |
| 50 | 228.00 | 20.00 | 2.00 | 218.00 |
| 60 | 248.00 | 20.00 | 2.00 | 238.00 |
| 70 | 268.00 | 20.00 | 2.00 | 258.00 |
| 85 | 296.00 | 28.00 | 1.81 | 282.00 |
| 100 | 325.20 | 29.20 | 1.94 | 310.60 |

Table XXXVII
Acid Correlation
Run E-1

| Time in Mins. $\theta$ | Acid yield A | Change in yield $\Delta A$ | Rate of change of yield $\Delta A/\Delta\theta$ | Average yield A avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 5 | 262.00 | 262.00 | 52.40 | 131.00 |
| 10 | 363.00 | 101.00 | 20.20 | 312.50 |
| 15 | 460.00 | 97.00 | 19.40 | 410.50 |
| 20 | 524.00 | 64.00 | 12.80 | 492.00 |
| 25 | 581.50 | 57.50 | 11.50 | 552.75 |
| 30 | 631.00 | 49.50 | 9.90 | 606.25 |
| 40 | 725.00 | 94.00 | 9.40 | 678.00 |
| 50 | 815.00 | 90.00 | 9.00 | 770.00 |
| 60 | 906.00 | 91.00 | 9.10 | 860.50 |
| 70 | 1020.00 | 114.00 | 11.40 | 963.00 |
| 85 | 1135.00 | 115.00 | 7.67 | 1077.50 |
| 100 | 1256.00 | 122.00 | 8.12 | 1196.00 |

Table XXXVIII
Methanol Correlations
Run E-1

| Time in Mins. $\theta$ | Methanol yield M | Change in Methanol $\Delta M$ | Rate of change in yield $\Delta M/\Delta\theta$ | Average yield M avg. |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 5 | 9.23 | 9.23 | 1.85 | 4.61 |
| 100 | 76.18 | 66.95 | .70 | 42.70 |

Table XXXIX
Yields based on 1000 grams of Charge
All weights in grams

| Run | Average Temperature °C | Charcoal yield | Distillate yield | Acid yield as Acetic Acid | Methanol yield | Gas and * Loss |
|---|---|---|---|---|---|---|
| C-2 | 247 | 788 | 131 | 31.5 | | 81 |
| A-4 | 260 | 736 | 153 | 39.7 | 13.0 | 111.0 |
| B-2 | 288 | 573 | 199 | 51.0 | | 228.0 |
| D-1 | 337 | 442 | 330 | 92.2 | 49.1 | 228.0 |
| E-1 | 385 | 300 | 325 | 75.4 | 76.2 | 375.0 |

* Calculated by weight balance

TABLE XL

Calibration of Meters

Orifice Meter Number One
January 12, 1948
Temperature - 21 degrees centigrade

| Reading on manometer in cm. of ethylene dibromide | Cubic feet of nitrogen passing the orifice per second |
|---|---|
| 1.0 | 0.0076 |
| 2.0 | 0.0105 |
| 3.0 | 0.0115 |
| 4.0 | 0.0150 |
| 5.0 | 0.0160 |
| 9.0 | 0.0200 |
| 15.0 | 0.0295 |

Orifice Meter Number Two
January 12, 1948
Temperature - 21 degrees centigrade

| Reading on manometer in cm. of ethylene dibromide | Cubic feet of nitrogen passing orifice per second |
|---|---|
| 1.0 | 0.0082 |
| 2.0 | 0.0114 |
| 3.0 | 0.0141 |
| 4.0 | 0.0170 |

Capillary Meter
February 16, 1948
Temperature - 20 degrees centigrade

| Reading on manometer in cm. of acetylene tetrabromide | Cubic feet of nitrogen passing meter per second |
|---|---|
| 5.0 | 0.0076 |
| 8.4 | 0.0102 |
| 12.5 | 0.0125 |
| 20.0 | 0.0162 |
| 22.5 | 0.0172 |
| 3.0 | 0.0205 |

## Moisture Determination

Approximately 0.5 grams of sawdust were weighed into porcelain crucibles and placed in a constant temperature oven maintained at 105 degrees centigrade. After 8 hoursthe samples were removed and placed in a calcium chloride dessicator to cool. The samples were then weighed and the results obtained are summarized below:

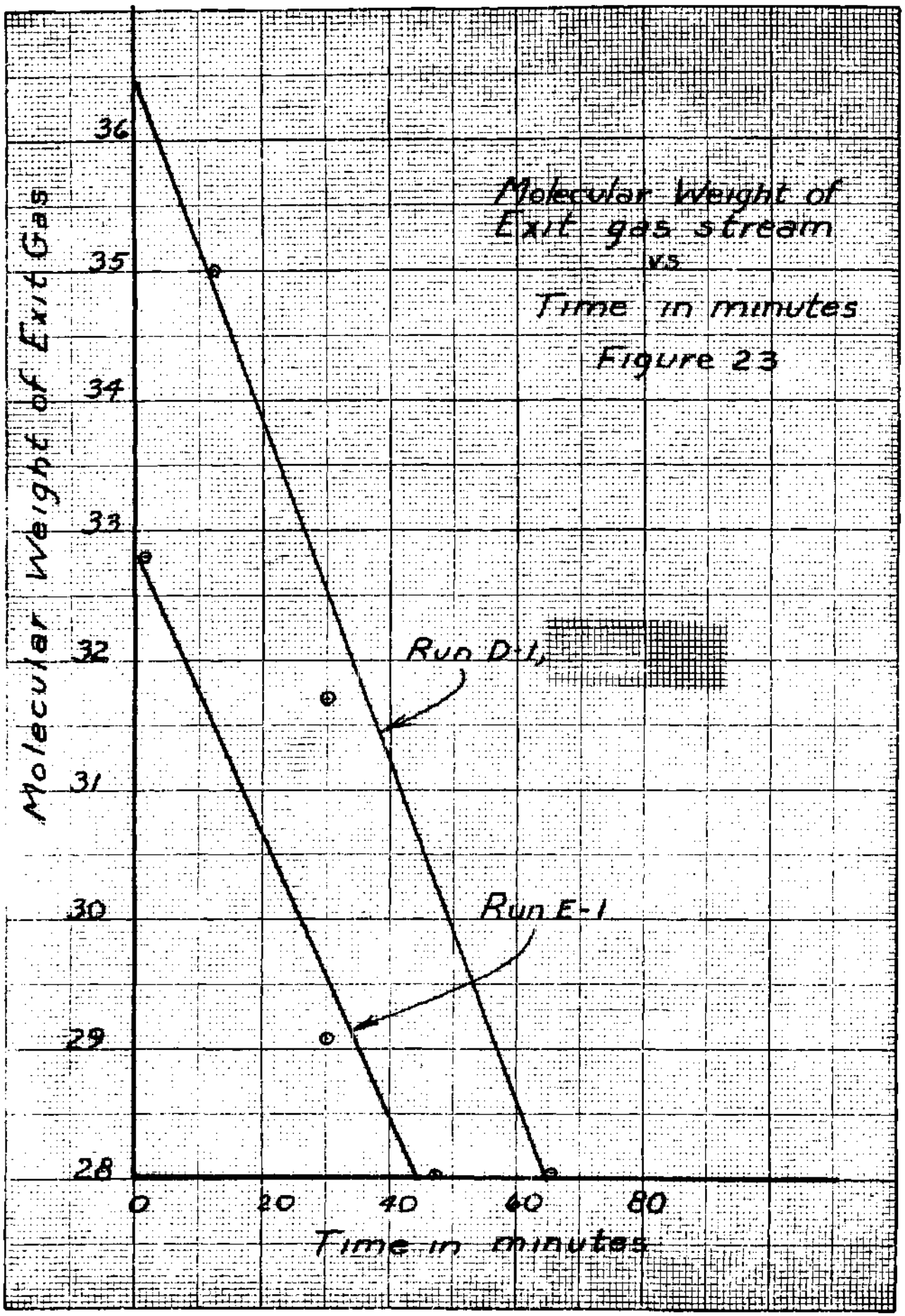
Weights before drying

| | Sample #1 | Sample #2 |
|---|---|---|
| Gross weight | 14.0722 | 10.2560 |
| Crucible weight | 13.5722 | 9.7560 |
| Net Weight | 0.5000 | 0.5000 |

Weights after drying

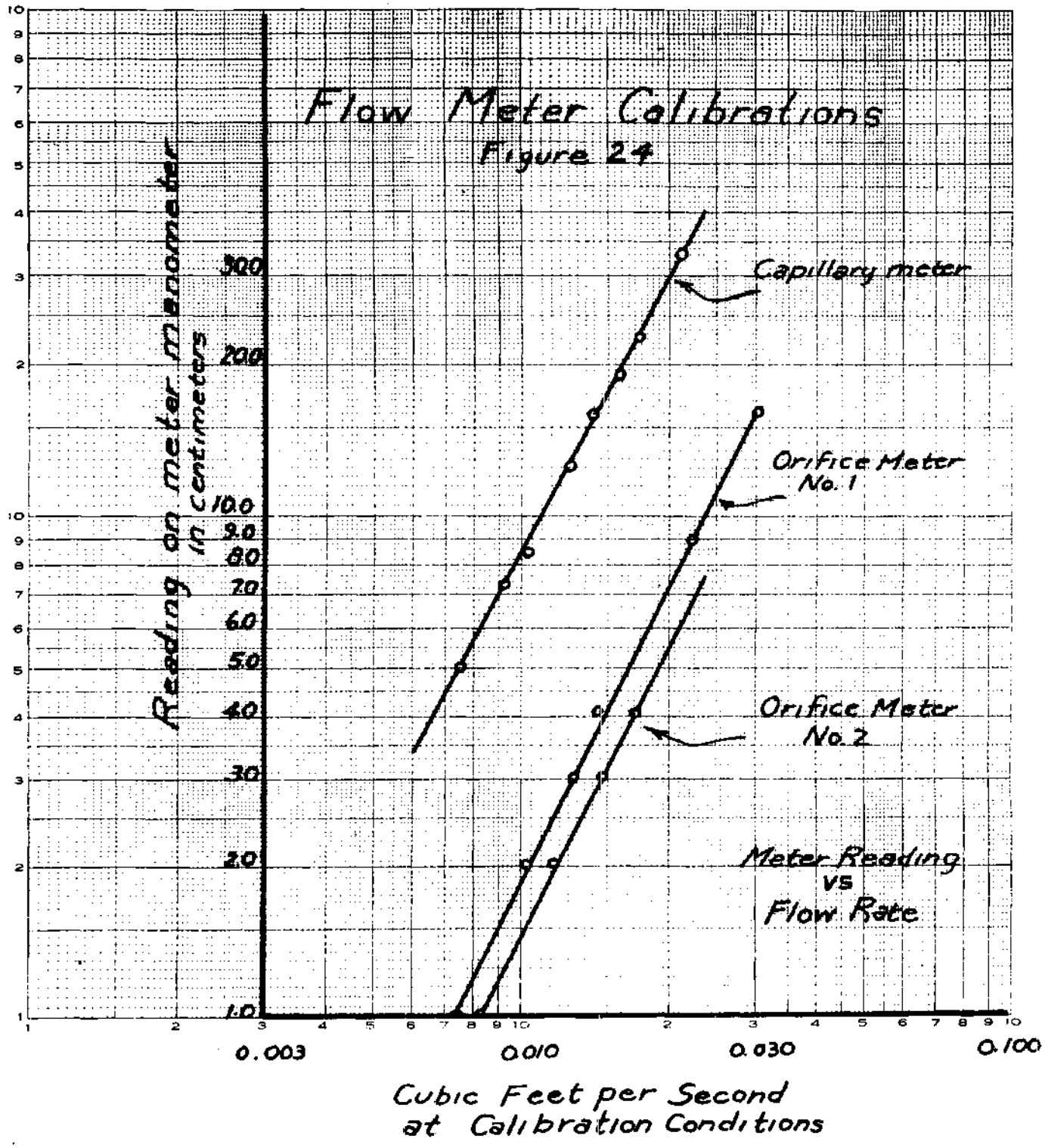
| | | |
|---|---|---|
| Gross weight | 14.0396 | 10.2246 |
| Crucible weight | 13.5722 | 9.7560 |
| Net weight | 0.4674 | 0.4686 |
| Percent loss | 6.52% | 6.28% |

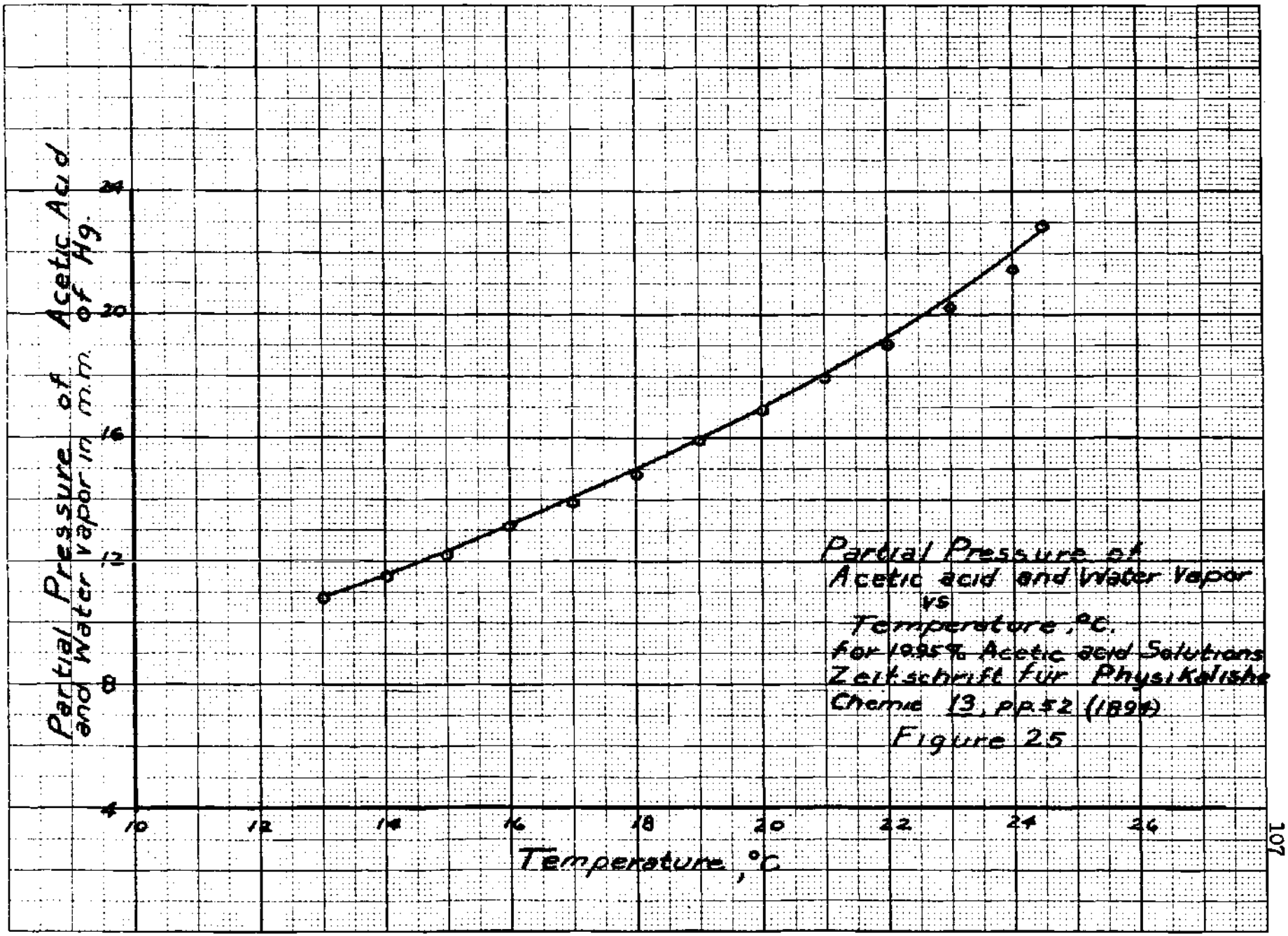
Average - 6.40%



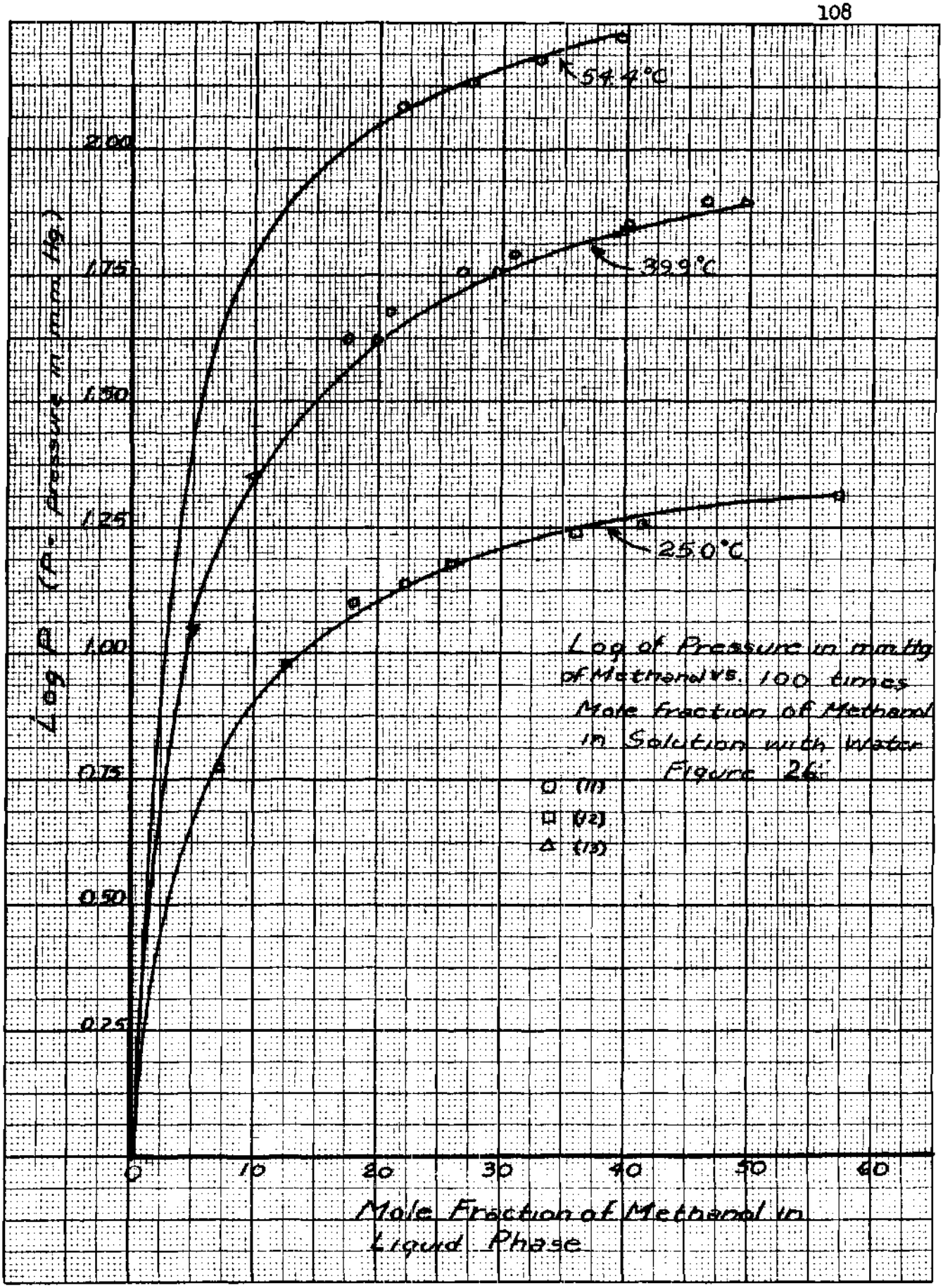

Molecular Weight of Exit gas stream
vs
Time in minutes

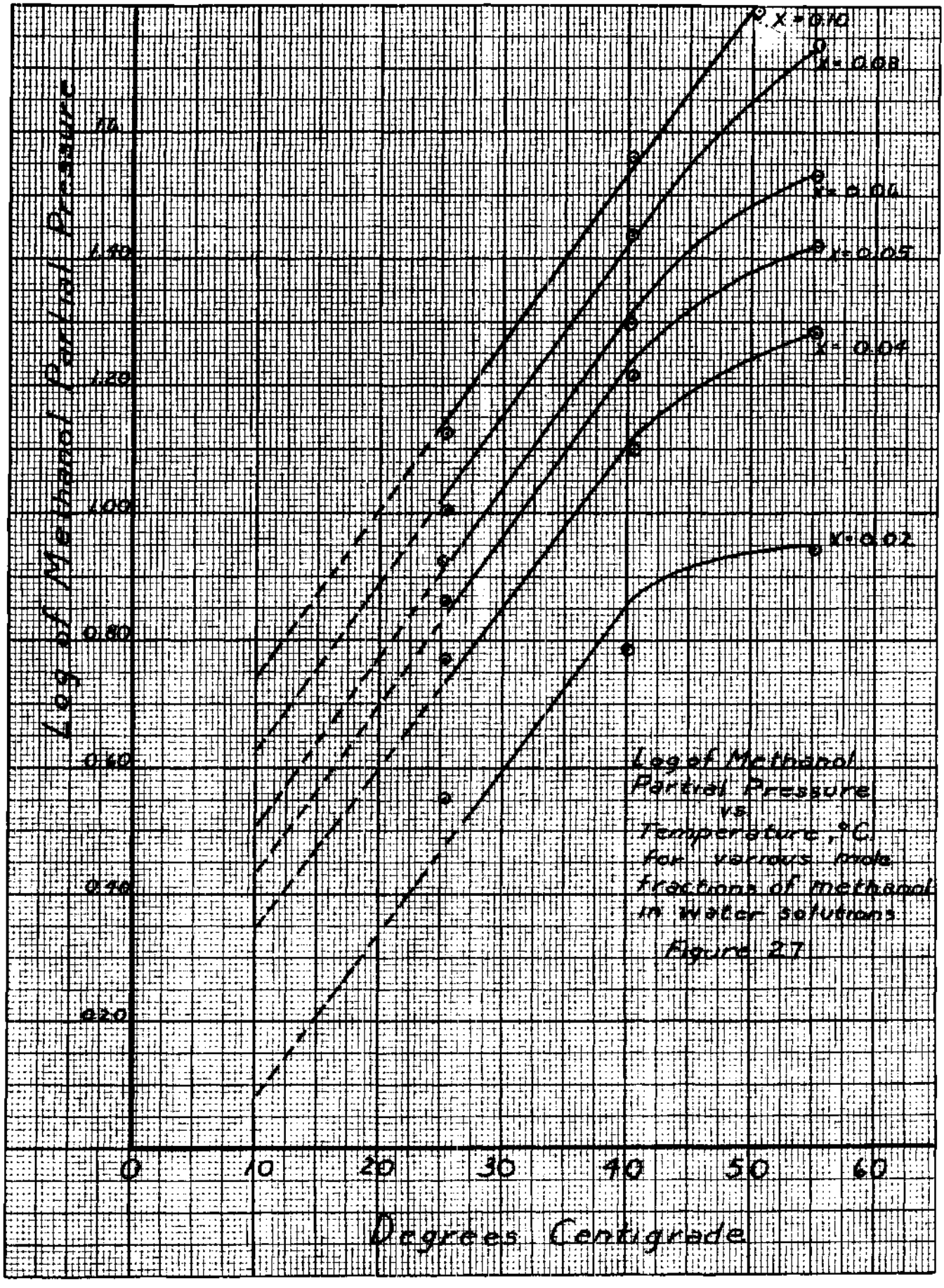
Figure 23


Flow Meter Calibrations
Figure 24
Capillary meter
Orifice Meter No. 1
Orifice Meter No. 2
Meter Reading vs Flow Rate
Reading on meter manometer in centimeters
300
200
100
90
80
70
60
50
40
30
20
10
0.003
0.010
0.030
0.100
Cubic Feet per Second at Calibration Conditions




Partial Pressure of
Acetic acid and Water Vapor
vs
Temperature, °C.
for 19.95% Acetic acid Solutions
Zeitschrift für Physikalische
Chemie 13, pp 52 (1894)
Figure 25


54.4°C
39.9°C
25.0°C
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
Log (P. Pressure in mm Hg)
0
10
20
30
40
50
60
Mole Fraction of Methanol in Liquid Phase
Log of Pressure in mm Hg of Methanol vs. 100 times Mole fraction of Methanol in Solution with Water
Figure 26
○ (11)
□ (12)
△ (13)




Log of Methanol Partial Pressure vs. Temperature, °C. for various mole fractions of methanol in water solutions

Figure 27

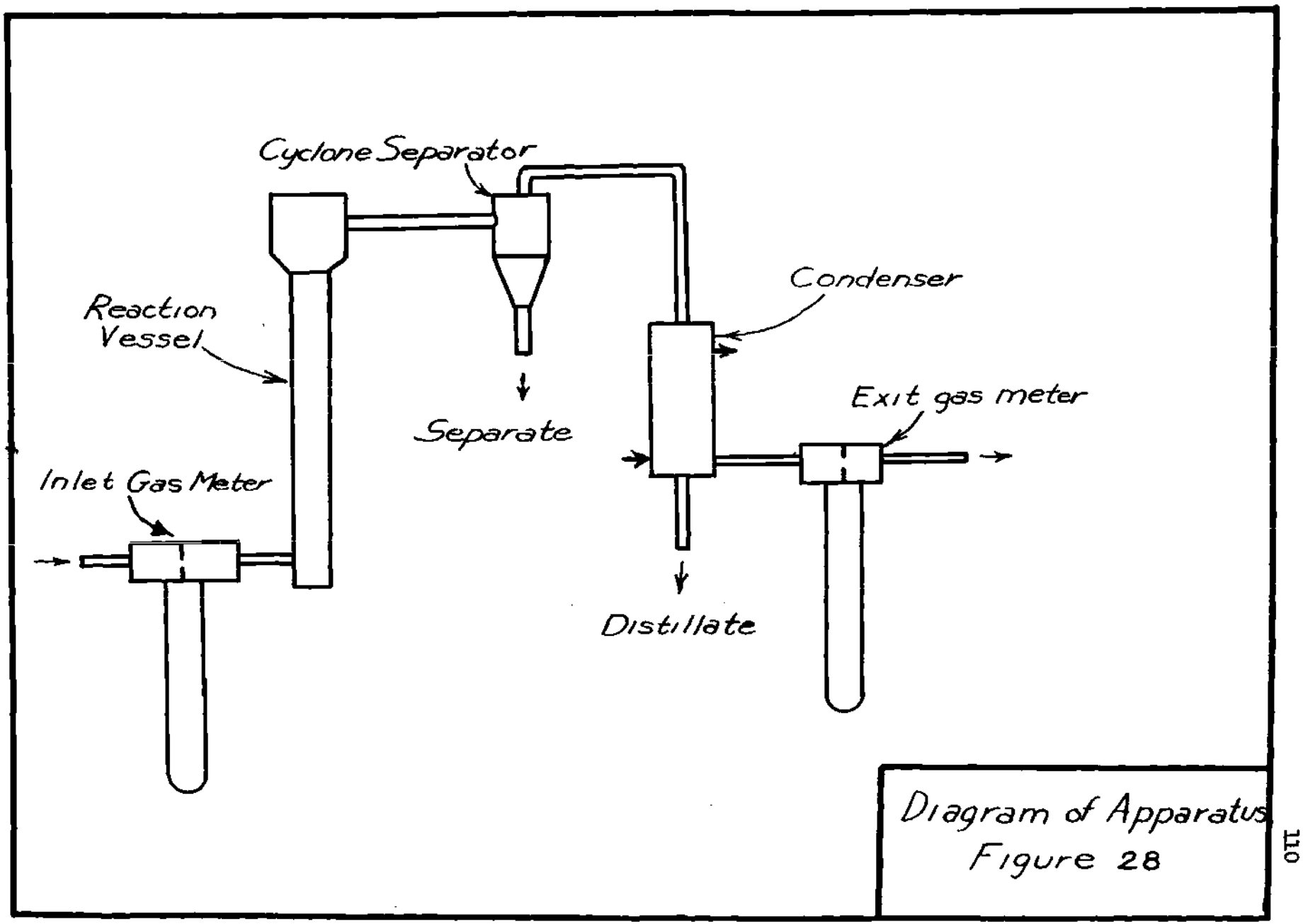



Diagram of Apparatus
Figure 28